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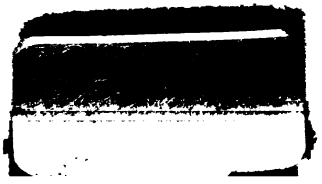

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CHEMISTRY IN THE HIGH SCHOOL

PARTS II AND III

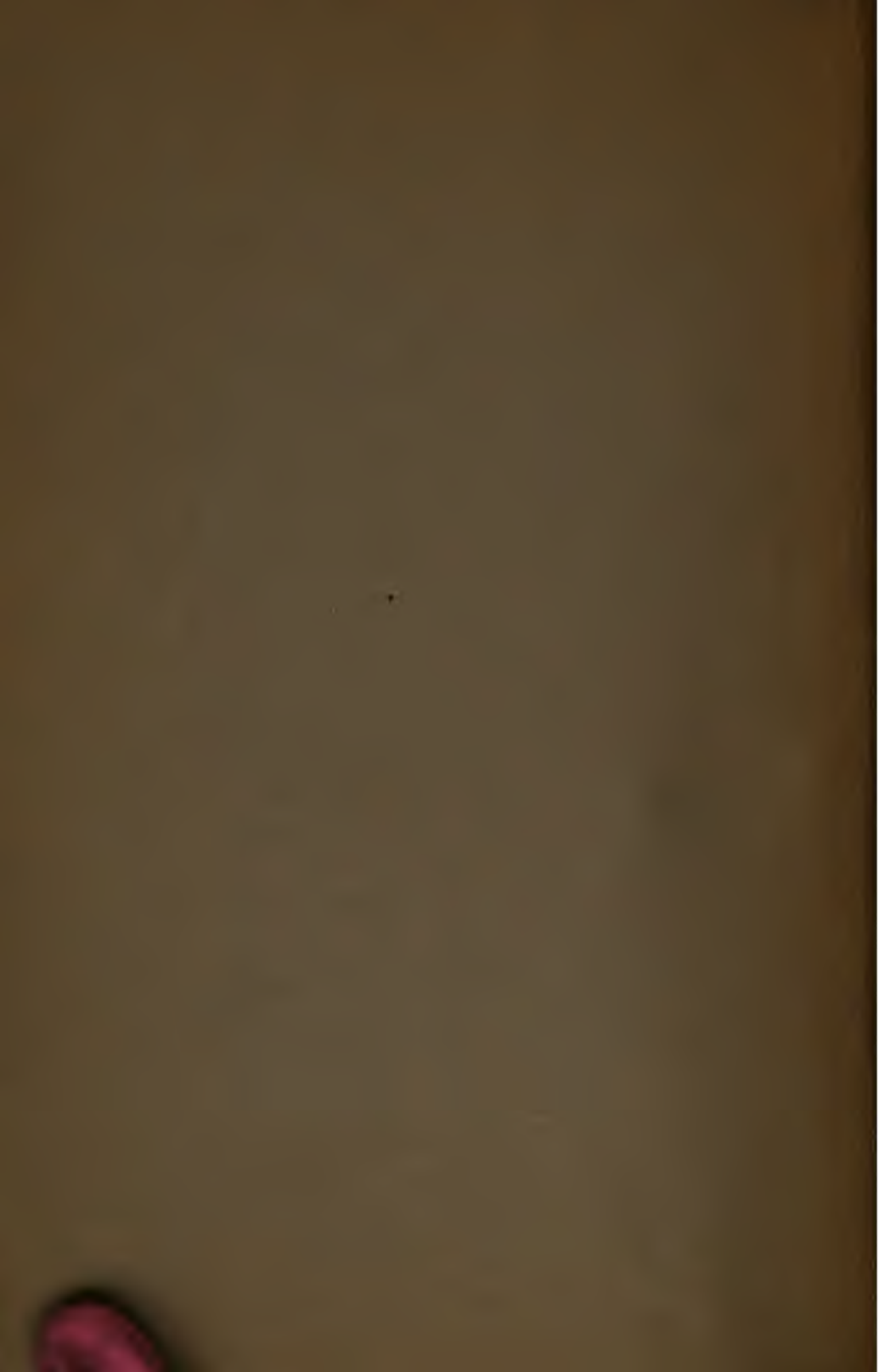
BY

E. P. SCHOCH, Ph. D.

PROFESSOR OF PHYSICAL CHEMISTRY
THE UNIVERSITY OF TEXAS

Published by the University six times a month and entered as second class matter at the postoffice at Austin, Texas

1914



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BULLETIN

OF

THE UNIVERSITY OF TEXAS

NO. 329

OFFICIAL SERIES NO. 100 APRIL 15, 1914

CHEMISTRY IN THE HIGH SCHOOL

PART I: EQUIPMENT

(PARTS II AND III TO FOLLOW)

BY

E. P. SCHOCH, Ph. D.,

Professor of Physical Chemistry, The Universiey of Texas

Published by the University six times a month and entered as scond class matter at the postoffice at

AUSTIN, TEXAS

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The benefits of education and of useful knowledge, generally diffused through a community, are essential to the preservation of a free government.

Sam Houston.

Cultivated mind is the guardian genius of democracy. . . . It is the only dictator that freemen acknowledge and the only security that freemen desire.

Mirabeau B. Lamar.

THE UNIV
CALIFORNIA

CHEMISTRY IN HIGH SCHOOLS.

INTRODUCTION.

Why Chemistry Should be Taught in High Schools.—Today our home life, our commerce, and the practice of our trades and professions involve chemical operations so frequently and require so much knowledge of the composition and properties of substances that the acquisition of such knowledge by young people is really a prime necessity. A course in chemistry can give such information. Of course, *training* is the first object of all school work, but in the study of chemistry training can be given while information of practical value is given. General facts and principles can be illustrated with materials met in daily life as well as, if not better than, with substances rarely met with. A course in chemistry can include more information of practical value than probably any other high school course, and if properly conducted the chemistry course will serve to train young minds just as well as any course primarily designed for this purpose. The study of chemistry gives young people much that is essential in all walks of life and it is an absolute necessity for the great number who deal directly with materials such as painters, builders, merchants, farmers, housekeepers, etc.

How to Secure a Modern Practical Course in Chemistry.—The high school chemistry course as generally given up till now does not attain the above object as nearly as it can be obtained by a course specially designed with this in view. This has just been recognized by a great many chemistry teachers, and the effort to change the chemistry courses in accordance with this idea has just begun. Naturally it is very difficult to introduce such a course at this time because there are no text-books on the market which really fit these peculiar conditions. Hence all teachers, even those who are otherwise well prepared in chemistry, must be allowed extra time for planning and executing a course along the new line. With this explanation it is clear that the following is necessary to secure a modern course in chemistry: A competent teacher; a proper allowance for the teacher to plan his course and to prepare his teaching and laboratory notes; a properly equipped laboratory.

This bulletin has been issued in order to help the high schools of Texas to attain these ends. It will consist of three parts, which

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WHAT SOME OF OUR SMALLER TOWNS HAVE DONE FOR CHEMISTRY.

Chemical Laboratory, Winnsboro (Texas) High School.

Chemical Laboratory, Corpus Christi (Texas) High School.

WHAT SOME OF OUR SMALLER TOWNS HAVE DONE FOR CHEMISTRY.

Chemical Laboratory, San Marcos (Texas) High School.

Chemical Laboratory (on left), Eagle Lake (Texas) High School.

will treat, respectively: (1) equipment, (2) exercises for student's use, and (3) a teacher's manual to accompany the exercises.

The University of Texas Requirements for One Unit Entrance Credit.—The University of Texas has recognized the wisdom of designing courses for elementary chemistry so as to benefit the future citizens in all walks of life. It is co-operating with the Texas State Teachers' Association in their efforts along this line, and it conducts its elementary course in chemistry with this aim in view. Hence in the preparation of this bulletin a special effort has been made to furnish aids for the design and conduct of a high school chemistry course which seeks to attain these ends.

While the University hopes in this way to aid high schools in securing the most valuable kind of a chemistry course, it will not limit its acceptance for affiliation credit merely to courses conducted along this line, but it will accept any courses which meet the following general requirements:

1. A properly prepared teacher.
2. A proper class time allowance. The time spent in the class must not be less than three recitation periods of forty-five minutes and two laboratory periods of ninety minutes a week for one year.
3. A fairly well equipped laboratory in which the students do individual work.
4. Some evidence that the teacher occupies the time with a well-planned and well-conducted course. This evidence is obtained by a personal visit of an official and an inspection of the note-books and examination papers of the students in the course. The examination questions and the note-books have been found to be very good indicators of the preparation of the teacher, and of the time and thought he spends in planning the course, selecting suitable topics, and conducting the course; for affiliation credit it is not only the student's work that is to be judged, but first of all the teacher's work and his ability. Little or no attention is paid to the text-books used because a well prepared teacher can give a good course even with a poor text, and a poorly prepared teacher may not succeed even with an excellent text. The mere following of a text will always produce a course of relatively low value, while for the future development of the State first-class high school chemistry courses are absolutely necessary.

PART I—EQUIPMENT.

The Teacher.

First and most important is the teacher. He should be above all a *science* man, both by inclination and training,—a person whose inclinations and desires naturally make him fond of the subject. He should have had some sound training in chemistry and he should have received this training at a place where this subject is taught *extensively* rather than at a place where only introductory work is given, since much necessary information is absorbed from the proper "atmosphere." The extent of the person's training in chemistry should not be less than two thorough courses in a first-class college or university, and in addition some college training (at least one course) in either physics or in a biological subject (botany or zoology). This minimum requirement is not excessive, and frequently persons may be obtained who have had much more training than this.

Attention should be called to the fact that the courses which a teacher may have had may supply very little information directly usable in a modern chemistry course to be given in a high school. This is particularly the case if, as frequently happens, the two college courses that a teacher has had presented descriptive inorganic chemistry, qualitative analysis, with perhaps some quantitative analysis. Very little of the information gained in such courses can be used directly in a modern high school course, and teachers who have had such training only should realize at the outset that they must learn another set of facts entirely—namely, the fundamentals of general or physical chemistry, the fundamentals of organic chemistry, and the fundamental chemical facts needed in industry, commerce, and home life,—so-called applied chemistry. A teacher who has not had any physical chemistry or who has not had organic chemistry, should study these subjects in college at his earliest opportunity. A teacher who knows the fundamentals of these subjects and makes a persistent effort to learn applied chemistry, will, if allowed time enough for the proper preparation of his course, be able to give a good course. With less preparation or with a different preparation, his task is very difficult for him; while without an ample time allowance for

the design and conduct of the course no teacher can give as good a chemistry course as should now be demanded or as may be reasonably expected.

When and Where to Order Laboratory Supplies.

The teacher who is to use the laboratory should design its equipment and order the materials.

The supplies should be ordered early in June. It is quite profitable to submit large orders to several of the large importing houses for quotations for *duty free* importation and *delivered at your railway station.* If the ordering is delayed beyond July 1st it will scarcely be possible to secure a duty free importation by the time the session opens in the fall. All of the large chemical dealers mentioned in the list below will import apparatus duty free if requested to do so.

C. H. Stoelting Co., successors to Chicago Laboratory Supply and Scale Co., 31-45 W. Randolph St.....Chicago, Ill.
Central Scientific Co., 20-28 Michigan St.....Chicago, Ill.
Edward P. Martin Co., 144-146 E. Erie St.....Chicago, Ill.
L. E. Knott Apparatus Co.....Boston, Mass.
Bausch & Lomb Optical Co.....Rochester, N. Y.
Woldenberg & Schaar, 1025 S. State St.....Chicago, Ill.
Eimer & Amend, 205-211 3rd Ave.....New York.
The Kny-Scheerer Co., 404 W. 27th St.....New York.
E. H. Sargent & Co.....Chicago, Ill.

Selection of a Room for the Laboratory.

In the selection of a room for the chemical laboratory the following requirements must be met:

The room must have such means of ventilation that all fumes may be removed rapidly and not blown into other parts of the building.

Communicating with the laboratory there must be a small room where the supplies may be kept under lock, and in which the teacher may prepare experiments and solutions.

The store and preparation room in turn must communicate with the class-room so that the setting up and removal of lecture apparatus may be facilitated.

If the teacher also teaches physics, then the store and preparation room, as well as the class-room, may be used for both subjects; but in that case the physical laboratory should be located conveniently near so that apparatus may be transferred to and from the storeroom without unnecessary trouble.

The simplest way to meet the requirement of an adequate draft is to select a room with outer walls and windows on at least two sides. If an inner room with only one exposure (south!) must be used, then there must be provided at the farther end of the room from the windows one or more ventilating shafts so located that all parts of the room may be swept by the air current coming in at the windows and passing out through the shafts. Such a shaft should be one to two feet in diameter, and it should extend straight to the top of the building. The cover or cap on the roof over the top of this shaft should be placed very high (say twelve inches) above the top of the shaft, so that it will not impede the draft. Cornice men frequently place this cap entirely too low. It is desirable to aid the draft by putting a gas flame or an electric fan at the bottom inlet.

The form of ventilators frequently employed for ventilating ordinary buildings (that is, narrow shafts extending up in the wall, and opening into the rooms by means of a series of holes near the ceiling of the room) provides *insufficient ventilation for a chemical laboratory.*

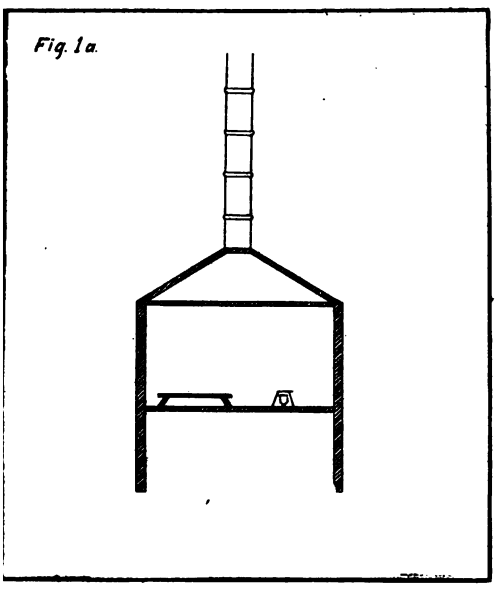
Draft Hoods.

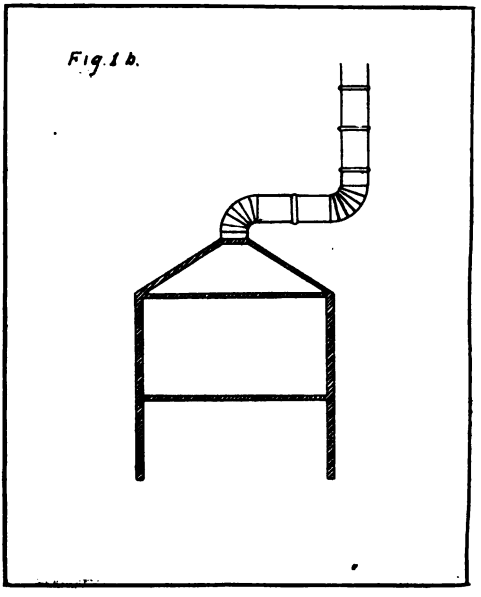
Obnoxious gases should not be allowed to escape freely into the atmosphere of the laboratory, but should be confined to special draft hoods. Such draft hoods must be carefully designed, otherwise they are worse than useless. The following rules should be observed in their design:

1. The hood should be as small as practicable. More and smaller hoods should be the rule.

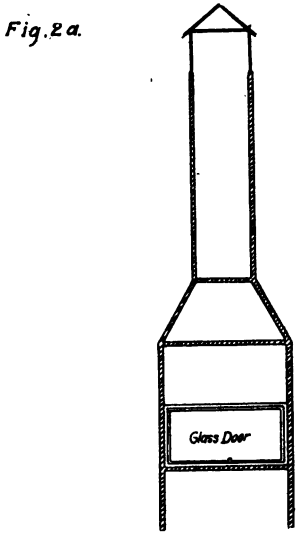
2. The stack should be vertical throughout its entire length.

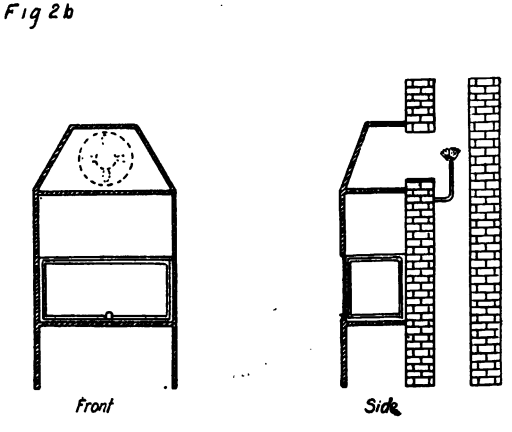
3. The hood proper, which is the part below the stack in which the apparatus is placed, should be as small as possible, so that the velocity with which the air moves through it may not be less than one-third of that with which it moves in the stack. The velocity of the draft should be great enough to lift the heav-





Examples of Faulty Hood Design.





Examples of Proper Hood Design.
From the *Chemical Engineer.*

iest vapors, as, for instance, those of sulphuric acid. The inlet for the draft should be placed so that the current of air from that point to the chimney may sweep through all parts of the hood. For this purpose some stops are usually placed so as to *prevent closing entirely* the front door of the hood. This carefully adjusted air inlet is essential to the successful operation of the hood. The hood proper should be made as low as convenience will permit in order that the length of the *slowly moving air column in the hood* may be as short as possible.

4. The stack or chimney should be proportionate to the size of the hood and its cross sections should not be essentially less than one-third of the cross section of the hood proper.

5. A large gas burner should be placed at the base of the stack at a point at which it is possible to light the gas by reaching up into the hood with a burning candle on a stick. This gas flame need not always be lit when the hood is used, but in quiet weather it must be lit in order to establish a sharp draft in the chimney.

6. A cap covering the stack for the purpose of keeping out rain is frequently not necessary and naturally the hood will operate best without the cap. Should a cap be found necessary, then care must be taken to place it very high above the top edge of the stack in order that the draft may not be impeded by it.

Hoods are frequently constructed without any consideration of the fundamental principles to be observed in order to get a good draft. Fig. 1-a shows a hood in which the stack is entirely too small. In Fig. 1-b, the stack suffers from the further impediment of not being straight. These mistakes in design are frequently found in actual hood construction. Fig. 2-a shows the ideal hood construction. In this hood the stack runs straight up from the closet and is large enough to provide for a sharp draft. Fig. 2-b shows a mode of construction in which the closet is built to connect with a large flue in the wall. If the *diameter of this flue is large enough* and a flame is placed as shown, then the hood will operate properly. All these figures show the form in which the hood proper, or closet, is generally built. The bottom of the closet is usually at the height of the ordinary laboratory desk and the height of the closet above the table to the

contracting portion is 30 to 36 inches. The sliding front door, as well as the two sides, should be made of glass.

Arrangement of Desks, Shelves, Etc., in the Laboratory.

In the placing of the laboratory desks and the supply shelves care must be taken to leave enough room for the students and instructor to pass each other and secure their supplies readily. The distance between the desks should be 4 feet 6 inches, certainly not less than 4 feet. Desks should not be placed adjacent to the wall anywhere, and a space at least 6 feet wide should be left between the wall and the desks all around the room. However, this space is large enough to place shelves along the wall wherever desired, as well as shelves for blast lamps, balances, and other special apparatus. It is advisable to place a platform with a suitable table and a blackboard in the room so situated that the instructor may make special demonstrations before the class or give special explanations while laboratory work is in progress. This provision is important because a great deal of the laboratory is conveniently done "class fashion."

In placing the desks, the manner of running the gas, water and sewer mains should be considered: It is most desirable to run these *underneath the ceiling of the room below* the laboratory—hence open to view and accessible for repairs at any time; this permits the placing of the desks in any way desired. If, however, the pipe mains must be placed *in the floor,* then they should run so as not to cross the floor joists, and the desks must be placed accordingly. The floors over the pipe mains should not be nailed down again, but made "trap-door" fashion.

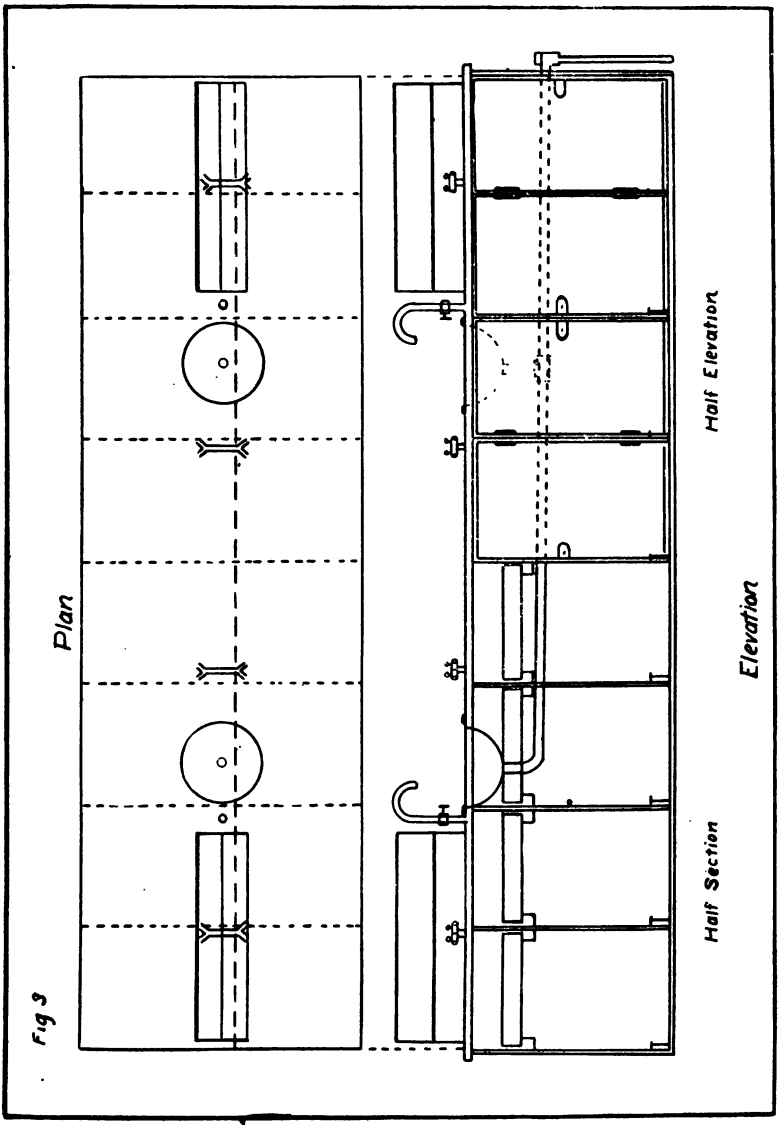
There should be *no high shelves* or other superstructure *on top* of the laboratory desks which would prevent the instructor from looking across the room and seeing what is on top of any desk. The sets of reagent bottles are to be placed on small, low, movable shelves, 36 to 40 inches in length, designed to hold one row of bottles on each side, with a partition at the center not over six inches high. The bottoms of the shelves should be six inches "clear" above the table top, but the total height of the shelf and bottles should not exceed 12 to 14 inches.

Details of Desks.

In most schools the laboratory is to be used by two sets of students on different days. This is easily arranged, because the amount of desk top space required by a student while working is large enough to construct two independent lockers underneath it. In the University of Texas such lockers have just been changed to two independent drawers each, so that the laboratory can be used by four different sets of students during different periods. The details of this arrangement are given below. It has been found to be a very practical arrangement and really better than the "two-locker" arrangement.

The table top space allowed per student, while at work, should be 42 inches in width, and 24 inches in depth. The desks should be 36 inches high. Each student should have for his use two gas cocks and between each of the two students working together there should be a water faucet and a sink. These should be placed in the center of the desks so as to be accessible from both sides, and hence be used by four students in common. The pipes run from one end of the desk underneath the top along the center of the desk.

Each locker should be closed by a large door hinged so that when open it may be folded back upon the unused locker. The lower part of the cupboard should be left open to a height of 26 inches, and in it should be placed a shelf 12 inches wide placed 8 inches above the floor in the back of the cupboard. In the upper part of the cupboard there should be a drawer the size of which, however, need not occupy the whole free space, which is 8 inches; instead, the drawer need be only 3½ inches high. The partition between the two sets of cupboards facing each other may be made of the cheapest sort of lumber boxing. It should be placed 2 to 3 inches "off center," so that the pipes may be placed along the center. The side partitions, that is, those at the ends of the desks and between the individual lockers, may be made of ceiling, the strips running vertically. The door also may be made of ceiling and the hinges should be placed so that screws cannot be drawn when the door is closed. Stout hasps should be supplied with which to lock each door. For further details of construction see Fig. 3. The tops may be made of



Chemical Laboratory Desk.

flooring; though it is advisable to make them of 1¼-inch white pine or cypress. The surface should be covered twice with a *half-saturated* solution of paraffin in gasoline, and it should be covered once at intervals of a year or so. This is a better surface treatment for these desks than most other "so-called acid proof" treatments. The solution is prepared by saturating some gasoline with finely sliced paraffin, and then adding an equal volume of gasoline to the solution.

As mentioned before, in place of the two lockers there may be supplied four drawers, each with a hasp and staple for locking them independently of each other. These drawers should be 19½ inches wide, 20 inches long and 12½ inches high (over all). The sides and backs of the drawers need not be more than half this height. A horizontal partition must be placed in each desk between the upper and lower drawer, but none below the lower drawer. The two drawers and the partition together take up only 26 inches of the total height of the desk, and leave an open space of at least 8 inches beneath the lower drawer. In these spaces are kept the iron ring stands and the funnel stands, one of each of these to be used in common by the four students who occupy the desk during different periods. All the rest of each student's outfit can be put into the one drawer assigned to him. Of course such tall objects as the wash bottle, the test tube stand, etc., must be so selected as not to exceed 11½ inches in height.

The desks should not be too long; 14 feet is the *maximum* length desirable; such a desk contains sixteen lockers, and top space for eight students working simultaneously, four on each side. It is advisable to make the desks only half as long, that is, with only four lockers to the side, and then to place sinks at the ends of the desks.

Plumbing.

It is unnecessary to "trap" each one of the sinks separately; the main pipe only needs to be trapped at some convenient point.

The desks should be so arranged that the main pipes pass up the center or one side of the laboratory so as to touch the end of each desk. Of course, the size of these mains depends on the number of desks. In the laboratory to which the accompanying figures refer, built to accommodate 236 individual lockers, the

sewer main is a cast iron pipe 4 inches in diameter, the water main is a 2-inch pipe and the gas main is a 2-inch pipe. The laterals for a sixteen-locker desk unit as used in this laboratory are of the following dimensions: drain pipe, 2 inches (cast iron); water and gas, 1 inch each. Where the drain pipe comes out of the desks and turns downward, a "T" should be placed instead of an elbow. By this means an obstruction in the pipe may be readily dislodged. Here the pipes should be joined by a *union* in order that a desk may be easily disconnected.

The sinks may be of porcelain; a 14-inch hemispherical bowl such as may be obtained for about one dollar, or a little above, will serve the purpose very well. It should not be fastened to the drain pipe, but the spout should merely extend into a short piece of lead pipe connecting with the drain pipe. Sinks placed at the ends of desks should be of rectangular form, lead lined, 16 by 20, and 10 inches deep inside. A water faucet of the ordinary *bar-fixture* type, will be found suitable. When in use a short piece of rubber tubing should be attached to the faucet to prevent any splashing of water.

The gas cocks should be chosen carefully so as to fit the size of rubber tubing used on the Bunsen burners. The gas cocks commonly used by plumbers for dwellings are *entirely too large* for this purpose.

Cost of Desks and Plumbing.

At present the cost of desks made according to this design is, in Austin, approximately $4.00 per locker. If two drawers are provided in place of each locker, the cost is approximately $5.50 for the same unit. The plumbing, including mains, etc., is about $1.50 per locker additional.

Other Furniture.

One or several hoods will be required. It is difficult to give an estimate of these because the cost depends entirely upon the design. However, the hood proper without the stack need not cost more than $15 to $18.

The storeroom and the teacher's work room should be supplied with large, commodious, plain shelves, for the stock of supplies,

etc. Placed in a separate, well-closed small room, as they should be, they need no doors to keep out the dust, and such open cupboards are much more practical than closed cupboards. The teacher's room should also have a commodious table supplied with gas, and a large sink.

Other Desk Designs and Ready-Made Desks.

In many schools individual desks are now used, and they are arranged so that all the students face in the same direction. Furthermore, a space is left beneath them so that a student can sit conveniently upon a stool while doing his work. Such a desk can be readily designed by taking the space occupied by two cupboards in the former design, adding to it about 20 inches for the open space beneath where the student puts his feet in sitting, thus making a unit of 62 inches width, about 30 inches depth and 36 inches height. The two cupboards are placed on the two sides with the central open space between them. The water, gas and sink may be placed anywhere on the back part of the desk, though they are usually placed in the space between the two lockers and as near the back edge of the top as is possible. The cost of this construction is necessarily greater than that mentioned above. Inclusive of plumbing, it cannot be less than $20 per desk with two lockers, even if it is constructed as cheaply as possible.

Frequently school authorities not wishing the trouble of constructing desks, desire to secure them ready made from some reliable business firm. Desks built by manufacturers, who make a specialty of such work, present many points of advantage; they are generally well designed and well made. Naturally their cost will be much greater than the cost of the simple desks mentioned above. The following parties make a specialty of manufacturing laboratory furniture, and it is advisable to obtain the catalogues of several houses while studying this matter:

The Kewanuee Manufacturing Co. (Catalogue No. 4), Kewaunee, Wis.

Leonard, Peterson & Co., 1240 Fullerton Ave., Chicago, Ill.

L. E. Knott Apparatus Co., Boston, Mass.

The *best design of an individual desk* found on the market is

that of the Altaffer Individual Desk, which is designed and manufactured by L. B. Altaffer, 1445 Wyandot Ave., Cleveland, Ohio.

Laboratory Burners and Fuel Supply.

The *alcohol lamp* is so feeble that nearly all teachers agree in reporting it as *absolutely unsatisfactory.*

The small gasoline torch sold by all dealers (e. g., Central Scientific Co., Cat. No. 4449), is reported as quite satisfactory by some teachers and as unsatisfactory by others. The difference in opinion is probably due to the fact that the valves of the pump do not last longer than one session and then give much trouble; again, the gasoline must be filtered through a chamois bag, since otherwise the small gasoline vent in the burner is choked up frequently. Usually repairs have to be made by the teacher, hence with heavy laboratory work, and more than a few students, the loss of time caused by these burners *becomes prohibitive.*

The valveless gasoline burner (e. g., Central Scientific Co., Cat. No. 4455) is rather feeble and exceedingly troublesome, hence it is not to be recommended.

Acetylene gas may be burned in a Bunsen burner of special construction (Central Scientific Co., Cat. No. 4632). It is a very convenient and satisfactory source of heat, but its cost appears to be prohibitive.

Gasoline Gas Machines.—There are at least three distinct machines of this sort on the market: the F-P gas machine, sold in this State by the Texas Lighting Co., Box 687, Dallas; the Standard Vacuum gas machine, manufactured by the Standard-Gillett Light Co., 9-11 West Michigan St., Chicago, and the Tirrill gas machine, manufactured by the Tirrill Gas Machine Ltg. Co., 509 Fifth Ave., New York. See also the home-made machine farther on.

The smallest unit of the F-P. gas machine is for five burners, and the prices up to the fifteen burner size are much smaller that the price of the smallest unit (twenty-five burners) of the cheaper one of the other machines; but for a larger number of burners the others are at least as cheap, when all is considered, and they are certainly to be preferred. The writer has not seen the F-P machine in operation, but he really doubts that it is

suitable for chemical laboratories because the burners are permanently attached to the supply pipes, and the number of burners can be increased only by having the makers put in the additional equipment.

The two other gas machines, the Tirrill and the Standard Vacuum, are practically of the same type, and of quite a different type from the F-P machine. Of the Tirrell machines there are several now in successful operation within the State. Both machines are furnished in several sizes, the smallest of which furnishes gas for twenty-five lights. As quoted to the writer, the price of the Standard Vacuum machine is considerably less than the price of the Tirrill. Attention must be called to the fact that the prices for these machines are f. o. b. factories, and that the cost of their installation is considerable.

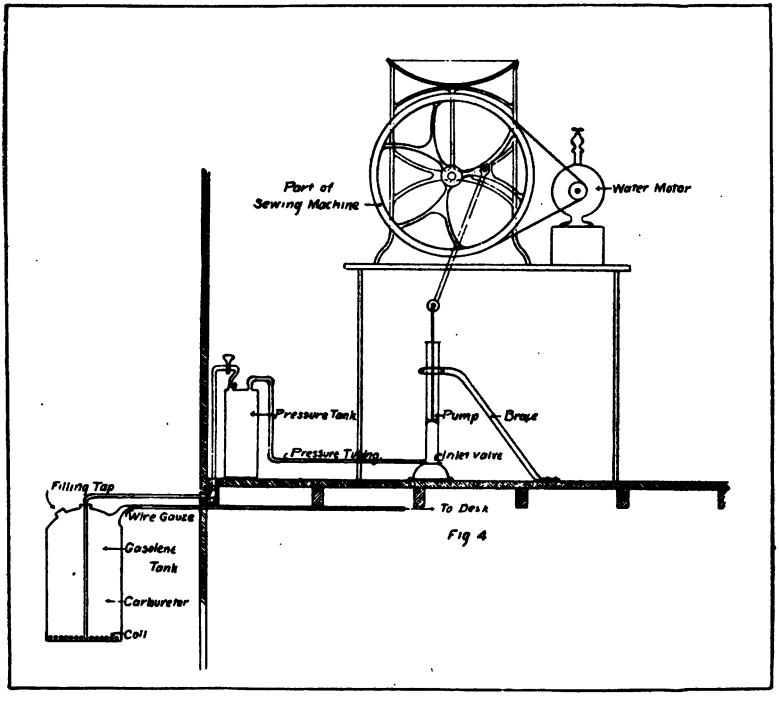
Although the purchase of one of these machines may appear to be an unduly large expenditure for this one need, namely, that of fuel, yet it must not be forgotten that these machines furnish the best fuel for laboratory purposes and save on other expenses, first of all on the cost of the burners, and, second, in saving the time which is otherwise lost by both the teacher and the pupil in keeping the other kinds of lamps in operation. Hence for a class of twenty or more a machine of this sort is much more economical than a number of gasoline blast lamps plus the cost of time for their operation. But even for smaller classes, for instance, of ten students, the extra expense involved in the purchase of such a machine will be balanced by the saving in several years.

A Home-Made, Inexpensive, Gasoline-Gas Machine.

A home-made, inexpensive gasoline-gas machine was installed in the Mexia high school last summer, and it has been in successful operation during the fall. Mr. A. G. Koenig, who designed and installed it, has kindly furnished the following description of it:

The gasoline-gas machine now in use in the Mexia high school consists of four parts: 1. The pump. 2. The air tank. 3. The carburater and gasoline tank. 4. The source of power. These are assembled as shown in Fig. 4. The pump used is one having

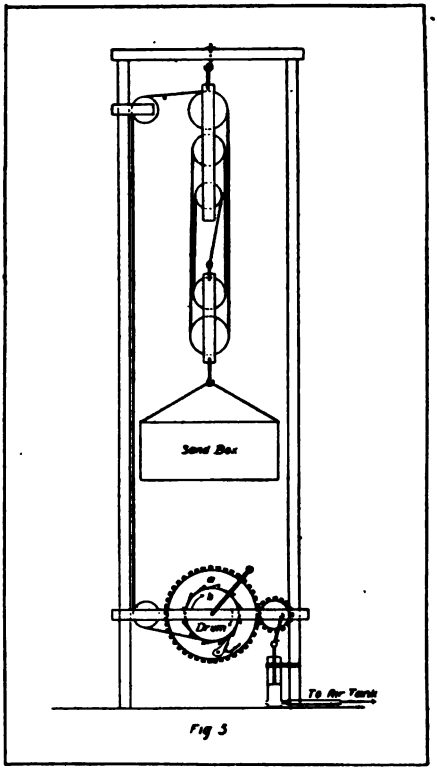
an internal diameter of 1.12 inches, the stroke is about 4 inches, and running at the rate of 150 strokes per minute it furnishes about one-fourth cubic foot of air per minute, which is enough to supply 12-15 Bunsen burners with gasoline gas. This pump was obtained from the Columbia School Supply Co., Indianapolis, Ind., at $4.90. The air tank is a No. 1827 pressure tank sold by the Columbia School Supply Co. for $3.75.



A Home-made Gasoline Gas Machine.

The carburater consists of a five-gallon oil can which can be bought for 60 cents, and about three feet of ¼-inch lead tube closed at one end and coiled up in the bottom of the can as shown in the diagram. A large number of very fine holes were made in this lead coil by means of a sewing needle or a fine awl. The air passing through these numerous holes in the coil at the bottom of the gasoline becomes saturated with gasoline vapor. It is

advisable to place two rolls of wire gauze in the iron pipes conveying the gas from this carburater to the laboratory; this prevents the flashing back of the flame through the pipes. Instead of the ordinary Bunsen burner it is advisable to use one in which the air and the gas supplies may be independently and accurately regulated. The expense for gasoline during the past three months has been about one cent per hour for ten burners.



Mechanical Power for Gas Machine.

The air pump is driven by a 6-inch water motor manufactured by the Divine Water Motor Co. of Utica, N. Y., price $5.00. The pulleys and mechanism for applying the power to the pump were obtained by adapting the foot power mechanism of an old sewing machine at a cost of $2.00.

There would be no difficulty in substituting a small electric motor (say a strong fan motor) for the water motor above.

Where neither electric nor water power is available the following device may be used as a source of power: A derrick consisting of four 2x4 scantlings, well braced, and about twenty feet high is used to raise a strong box filled with sand or other heavy objects. In order to have enough rope or wire cable to wind on the drum, a system of pulleys, consisting of three or four fixed at the top and two or three at the bottom, is used. This will give 100 or 140 feet of rope to be wound on the drum. The mechanism of the whole device is shown in Fig. 5.

The large cog-wheel *a* and the drum *b* run on the same axle. The rachet *c* allows the drum to be turned from right to left in winding up the weight.

Source of Current for Electrolytic Work.

The direct electric current needed for electrolysis may be obtained from dry cells, or from a "direct current" lighting system,—by connecting the current through as many lights as are necessary to secure the amount of current needed (a 40-watt lamp will give about 0.3 ampere). An alternating current lighting system may be used almost as easily as a source of direct current for electrolysis by means of the following contrivance, which is easily made "at home." This apparatus is designed for a maximum steady current of about three amperes. The total cost of the material is about $3.50, and it can be made in one to two hours. It will be found cheaper, more convenient, and more serviceable than primary batteries or dry cells. Although a *pulsating* current is thus obtained, because one stroke of the alternating current is suppressed, yet this is just as serviceable for electrolytic work as a continuous current.

Secure a one-quart fruit jar or a similar vessel, and a strip of sheet lead about 3 inches wide and 10 to 12 inches long. Hang this lengthwise into the jar, along the wall, and clamp it in position by bending the upper end over the rim. Solder a connecting wire to this. Fasten a wooden cover (6x6 inches) on the top of the jar by means of pieces of wood nailed as cleats to the under side of the cover. Secure by mail, from the U. S. Aluminum Co. (Pittsburg, Pa., or Old Colony Building, Chicago) rods of aluminum $\frac{1}{2}$ to $\frac{3}{4}$ inches in diameter and 10 to 12 inches long.

Specify the softest grade (Cat. No. *2SO*). Four rods ½x12 inches will cost 50 cents.

To fasten a copper connecting wire to the aluminum rods, drill, near one end of each, a hole large enough to admit the wire. When making connection insert the wire and clamp it by a few blows of a hammer on the side of the rod. Near the center of the cover, bore one (or two) holes of the exact size of the aluminum rods, so that the rods extending through these holes will be held in vertical position. Connect one wire from the alternating current main through a suitable number of lamps (as described above) and then to the lead pole of this "rectifying" cell, fill the jar with the solution of sodium phosphate prepared as stated below, and then the apparatus is ready for use; the aluminum pole serves as the positive pole of the direct current, and the other, free, wire from the alternating current main serves as the negative pole of the direct current.

The solution for this jar is prepared by dissolving one-half pound of sodium phosphate crystals in one quart of hot distilled water (or in rain water). A small amount of distilled water will have to be added from time to time to replace the water lost by evaporation. The solution need not be replenished often; only when it has become filled with a great deal of precipitate, and has become decidedly alkaline, then it will have to be changed.

The cell allows only that alternation of the current to pass which makes the aluminum pole the cathode, and it prevents the passage of the reverse alternation, which would make the aluminum the anode. This property of the cell is due to the fact that the aluminum is covered with a non-conducting film of aluminum hydroxide or basic salt with a gas (oxygen) held in its "meshes" or pores. Such a film over a metal does not prevent the passage of the current when this metal serves as the cathode; but it hinders the passage of the current when this metal serves as an anode. It is as though the cations need not actually touch the metal of the pole in order to be discharged, while the anions cannot be discharged unless they come in direct contact with the metal surface. Hence a cell in which one pole is covered with such an insulating film and the other not covered, or with a "conducting" surface, is "uni-directional" in its action.

Supplies.

These lists of apparatus and chemicals include all that is needed *in general* for high school chemistry work. Of course, special experiments are not provided for. The list calls for somewhat larger quantities than those given in some laboratory manuals, but these larger quantities will be found very desirable.

Individual Outfit.

Of each article in this list, secure enough to give every student and also the teacher a set. Furthermore, of the articles marked with an asterisk, secure at least 50 per cent more than is necessary for the individual sets.

1	burner, either a Bunsen burner with 2 feet of rubber tubing of best white rubber wrapped in cloth, diameter 11x6 (or a gasoline torch $2.75)	$ .50
1	wing top (for Bunsen burner only)	.10
1	iron stand (24 inches) with three rings	.65
1	iron burette-clamp and clamp-holder	.35
1	burette 50 cc. with glass stop-cock (See Note 1)	.70
1	deflagrating spoon	.03
*1	piece of wire gauze, iron, heavily tinned, 5x5 inches	.07
*1	piece of asbestos board 5x5 inches, $\frac{1}{8}$ inch thick (See Note 2)	.02
2	porcelain evaporating dishes, $\frac{1}{3}$ inch, $\frac{1}{8}$ inch	.25
1	small mortar and pestle of wedgewood, $3\frac{1}{2}$ to 4 inches in diameter	.40
*1	wash bottle (600 c.c.) with rubber stopper and glass tube fittings (See Note 3)	.30
*1	nest of 4 beakers—50 cc., 150 cc., 250 cc., 400 cc.	.40
1	crucible tongs	.50
1	porcelain crucible with lid, 18 cc.	.20
1	clay-covered iron triangle	.03
2	or 3 wide mouth (or salt mouth) bottles, 500 cc. (See Note 7)	.20
2	or 3 pieces of window glass, 4x4	.10
*12	test tubes, 16-160 mm., 1 cent each	.12
1	test tube rack with pins	.28

. 1	dropping funnel with cylindrical, open top, 50 cc. capacity; stem length, 12 cm., diameter 6 mm	.40
1	test tube holder (wire)	.08
2	glass funnels, 2½ inch and 3½ inch, respectively	.25
*1	test tube brush	.03
1	wooden funnel stand for two funnels	.60
1	triangular file (See Note 4)	.05
1	pneumatic trough (See Note 5)	.35
*½	pack (50) filter papers, 12½ cm. (5 inch)	.10
1	thistle top funnel tube, length, 12 in., diam. of stem, 6 mm.	.03
1	graduate, or one open top, graduated, cylinder, 100 cc	.15
*2	Erlenmeyer flacks *with two-hole rubber stoppers* to fit	.40
1	flask, 250 cc. with No. 3 or No. 4 rubber stopper; 1 flask, 400 cc. with No. 4 or No. 5 rubber stopper (See Note 6).	
2	watch glasses, 3 inch and 5 inch	.20
*3	gt. glass rodding, diameter, 3 mm., per lb	.50
*10	ft. glass tubing, diameters, 6x4 mm. or 5x3 mm., per lb.	.12
*2	hard glass test tubes of best hard glass, 18x160 mm	.20
1	porcelain spoon and spatula, length 10 cm., width of spoon, 14 mm	.10
1	piece of platinum wire, No. 28, B. & S. gage, length, 5 cm., fused into the end of a piece of glass *rodding*	.16
*1	piece of black rubber tubing, length 12 inches, diameters, 7x4 mm.	.20

Notes on Student's Outfit.

(1) All ground glass stop-cocks should be taken out and tied on the apparatus when not in actual use.

(2) This piece of asbestos board is to be used in place of a water bath, and for elementary work is much more serviceable. Should a water bath be absolutely required, then a large size beaker will probably serve the purpose. *No* water bath is included in the list.

(3) Buy 600 c.c. *Erlenmeyer* or Bohemian flasks, secure two-hole rubber stoppers to *fit mouth of flask* (probably No. 6 rubber stopper), and during one of the earliest laboratory periods teach the student how to make the glass tube fittings.

(4) Purchase the triangular files by the dozen from a local hardware dealer.

(5) Buy small dish pans and paint these inside and out with asphalt paint or with melted paraffin; they will serve the purpose just as well as the more expensive regular pneumatic troughs.

(6) These flasks with the rubber stoppers serve as generating flasks, as gas wash bottles, etc.

(7) Almost any sort of a wide mouth bottle (pickle bottle, fruit jars, etc.) may serve for these bottles. The pieces of glass to be used as covers may be supplied by a local dealer.

(8) All rubber ware, i. e., stoppers and tubing, when not in actual use, should be disconnected, or tubes drawn out of stoppers, etc., and should be laid away in the dark, since light decomposes rubber rapidly.

General Laboratory Supplies for a Class of Twelve Students.

One blast lamp and foot bellows for gas (or a large gasoline torch). There is no foot blower listed by American dealers that is as satisfactory and as lasting as the one listed by Dr. Bender and Dr. Hobein, Munich, Germany, Cat. No. 2201. The blower, No. 2, diameter 30 cm., is listed at 40 mark ($10) and is quite satisfactory. No. 2245, in the same catalogue, gives an extremely useful blast lamp (list price, $3.00) to be used with the blower. A blast lamp outfit is *not absolutely necessary* but is extremely desirable. By its means a teacher can make many pieces of simple glass apparatus, which otherwise is impossible. Simple glass blowing can and should be mastered by every teacher of chemistry. Helpful hints on glass blowing are found in the booklet: Shenstone, "The Methods of Gas Blowing." (Longmans, Green & Co.)

Six sets of eight desk reagent bottles, with labels blown in the glass capacity, 500 cc.; with ground glass stoppers (except where marked). (One set for every two students working simultaneously and one extra set for the teacher).

Concentrated Sulphuric Acid Dilute Sulphuric Acid Concentrated Hydrochlotic Acid Dilute Hydrochloric Acid Concentrated Nitric Acid Dilute Nitric Acid Ammonium Hydroxide Sodium Hydroxide (rubber stopper)	$10.92 for 6 sets.

50 to 75 solution bottles for the general side shelf in the laboratory; capacity, 500 cc., ground glass stoppers. To be labeled as desired, with paper labels.

For this purpose secure one or two label books (70 cents). The labels should be pasted carefully so that the paper will not "pucker up," the "gum" allowed to dry thoroughly, and then a layer of melted paraffin spread with a brush over the label, beyond the edges.

The salt-mouth bottles for the general supply shelf probably need not be purchased separately, as the bottles in which salts are shipped serve well for this purpose.

Balances for ordinary weighing, capacity 1000 grams. A very desirable balance is the Laboratory Balance, Cat. No. L 6010 (list price, $12), manufactured by Wm. Gaertner & Co., 5345 Lake Ave., Chicago. One such balance will suffice for ten students.

One set of weights, third class, 10 grams up to 2 Kg. (This balance has a sliding weight for the smaller weight down to 0.1 gram).

Water Still. If running water is at hand, a small automatic still (for instance, a *Jewell*) should be installed (one of capacity ½ gallon per hour will be ample for ten to twenty students). If the laboratory is not supplied with gas, a small (one-hole) blue-flame kerosene stove should be bought, and placed in position to heat the still. If running water is *not* available in the laboratory, a (5 gallon) copper retort (tin lined) and a block tin worm condenser may be used. It can be heated with a Fletcher radial gas burner or with a kerosene blue-flame stove. Either distilling

apparatus will cost slightly above $20. Two 5-gallon stout glass bottles for collecting and storing distilled water should be secured ($3.00), and one of them should be fitted with a glass syphon and pinch cock for drawing the water.

Two acid pots, stoneware, 3 gallons capacity, for diluting acids $2.00
3 sets of 3 smallest sizes of cork borers..... 1.50
1 set of 6 smallest sizes of cork borers..... .80
3 Kipps automatic gas generators, capacity 1 pint, with a broad base having a "tubular" in it for emptying the spent acid. For convenience in "filling," the tubular in the middle "globe" should be of 3½ cm. inner diameter.. 9.00
100 ft. tubing of soft glass, for bending, etc., diameter, 9½x12½ mm. ..... .85
30 ft. tubing of soft glass, for bending, etc., diameter, 14x18 .50
100 ft. tubing of soft glass, for bending, etc., 5 mm. outer diameter ..... .42
100 ft. tubing of soft glass, for bending, etc., diameter, 6x4.. .50
100 ft. tubing of soft glass, for bending, etc., diameter, 7x5.. .45
30 ft. soft glass rodding, 3 mm. diameter..... .15
10 ft. soft glass rodding, 6 mm. diameter..... .10
6 thermometers, solid stem, graduated up to 360° C..... 7.50
12 calcium chloride U-tubes, 6 inch, with side tubes attached . .72
12 Mohr's pinchcock clamps..... .98
12 screw clamps for compressing rubber tubing..... 3.00
6 lead dishes, 3 inches in diameter..... .75
12 distilling flasks, 250 to 300 c.c., with effluent tube half way up the neck. They are to be used in place of retorts. For a condenser, use a piece of soft glass tubing, diameter, 10x13 mm. Fit this over the side tube of the distilling flask by wrapping a strip of asbestos around the latter. When necessary place a wet towel around the condensing tube, or let this extend into a receiving flask submerged in water. To apply heat, place the distilling flask over a hole (1½ to 2 inches diameter) in a piece of asbestos board which is 5x5 inches in size. This prevents the flame from striking portions of the flask above the level of the liquid in it..... 1.50

2 large porcelain spoons..... .50
1 measuring cylinder, 1000 cc. open top..... .50
4 volumetric flasks without glass stoppers:
1—1000 cc. ..... .35
1— 500 cc. ..... .25
1— 250 cc. ..... .20
1— 100 cc. ..... .16
1 measuring cylinder, 1000 cc., glass stoppered..... .63
2 10 cc. pipettes..... .10
2 25 cc. pipettes..... .14
2 glass funnels, 6 inches diameter..... .40
4 porcelain evaporating dishes, ordinary form:
1—5 inches diameter..... .20
1—6 inches diameter..... .23
1—7 inches diameter..... .30
1—8 inches diameter..... .38
2 large porous cups and 1 rubber stopper to fit these—to be used for the demonstration of gaseous diffusion. A bell jar can probably be borrowed from the physical laboratory for this purpose.
Beakers of best Bohemian glass:
3 nests each, about 600 cc., 800 cc., and 1000 cc..... 1.80
1 package of 100 circular filter papers, 12 inches diameter .16
1 glass tube cutter (inside cutter) with extra cutting wheels. (E. & A. Cat. 3684)..... 1.25
1 filter pump (Aspirator), of brass, medium size..... 1.50
"Piccin" rubber cement, very convenient and useful for tightening joints and stoppers in apparatus. It is applied like sealing wax, but is preferable to the latter. Can be secured from Fritz Koehler, Leipzig, Germany, 4 pieces at 15 cents apiece, approximately..... .60
Cork stoppers, best quality—regular size.

	Diam. Small End.	
100	14	$ .38
100	16	.50
100	18	.60
100	20	1.00

50	22	.55
50	24	.60
50	26	.65
50	28	.75
50	30	1.00
50	32	1.10

Rubber Tubing.—Besides that necessary for the Bunsen burners and the black rubber tubing in the individual outfits, "for connections," secure the following:

Rubber tubing, white, best quality, wrapped in cloth,

Amount.	Diam.	
20 ft.	13x 7 mm.	$3.60
10 ft.	15x11 mm.	3.00

Balance for Quantitaiive Work.—This should be a balance in a glass case sensitive to a milligram. The capacity of the balance should be 300 grams, and a set of second (not third) class weights should be provided for it, and a supply of extra fractional weights should be on hand to replace any that may be lost. The balance shown in Eimer & Amend's catalogue No. 2122, and the set of weights No. 2198 (200 grams) are suitable for this purpose. In general, one such balance will be enough for seven or eight students only, hence if much of this work is to be done, two such balances should be provided for a class of twelve students. The price of such a balance and weights is about $20 to $25.

Special apparatus required for some of the experiments in the latter part of this Bulletin:

Porous earthenware cups, diameter 1.5 inches, length 3 inches, 20 @ 10 cents ..... $ 2.00

12 rubber stoppers to fit these cups, without holes (E. & A., size 7), @ 10 cents 1.20

2 pounds of lead wire (fairly pure lead; neither solder nor fuse wire will answer), No. 4 or 5 B. & S. wire gauge ..... .25

12 pieces of electric light carbons or graphitized carbon rods, ¼ to ⅜ inches diameter, 6 or more inches long .... .75

1 precision voltmeter (Western miniature precision direct current instrument), with two ranges, 25-2.5 volts 12.00

1 precision ammeter (same make as voltmeter above), with two ranges, 15-1.5 amperes..... 12.00
1 sliding rheostat, "Ruhstrat," wire wound on a tube, with connectors at both ends of the wire, and also one connecting with the slides, resistance 10-15 ohms, cappacity 6-10 amperes..... 3.00
3 drying towers or calcium chloride jars, on foot, with tubulure near bottom, 18-24 inches high..... .75

Chemicals for a Class of Twelve Students.

5 lbs. acetic acid glacial.....$1.02
18 lbs. hydrochloric asid c. p. in 6-lb. sealed bottles..... 2.16
7 lbs. nitric acid, c. p. in 7-lb. sealed bottles..... 1.00
2 lbs. fuming nitric acid..... 1.10
1 lb. oxalic acid, commercial..... .12
27 lbs. sulphuric acid, c. p. in 9-lb. sealed bottles..... 2.85
1 lb. tartaric acid..... .64
2 qts. 95 per cent alcohol..... .50
1 lb. ammonium carbonate..... .25
¼ lb. ammonium oxalate..... .12
1 lb. potassic alum..... .08
¼ lb. aluminum, filings or shavings..... .35
5 lbs. ammonium chloride, pure..... .90
¼ lb. ammonium sulphate..... .10
16 lbs. ammonium hydroxide in 4-lb. bottles..... 2.80
3 lbs. ammonium nitrate..... .70
8 ozs. antimony, powdered..... .25
4 ozs. arsenic trioxide..... .13
½ lb. asbestos wool..... .20
1 sq. yd. thin asbestos paper..... .10
2 lbs. barium chloride, crystals..... .25
¼ lb. barium nitrate..... .10
¼ lb. barium peroxide..... .35
1 oz. bismuth..... .30
1 lb. borax..... .18
½ lb. bromine in 2-oz. bottles..... .50
1 lb. calcium chloride, crystals..... .35
2 lb. calcium chloride, anhydrous, fused..... .80
1 lb. cadmium chloride..... 1.35

1 lb. calcium flouride	.10
Calcium oxide, buy locally	
¼ lb. cadmium nitrate	.40
1 lb. calcium nitrate	.80
½ lb. chrome alum, c. p	.25
1 lb. chloroform, Squibb's	.90
5 lbs. calcium sulphate, plaster of paris	.15
1 lb. carbon bisulphide	.16
10 lbs. calcium carbonate, marble chips	.50
2 lbs. bone black	.15
1 oz. cobalt nitrate	.15
1 doz. sticks willow charcoal	.36
1 lb. thin copper foil	.50
2 lbs. copper turnings, fine	.40
2 lbs. copper nitrate	.65
1 lb. copper oxide, black powdered	.75
5 lbs. copper sulphate	.50
2 oz. iodine, pure, crystals	.75
2 lbs. ferrous sulphate in 2-oz. bottles	.40
1 lb. ferric chloride	.12
2 lbs. iron filings	.10
5 lbs. iron sulphide	.35
2 lbs. sheet lead	.20
1 lb. lead nitrate	.18
1 lb. litharge	.12
1 lb. lead peroxide	.36
1 oz. litmus	.10
1 quire litmus paper, red	.50
1 quire litmus paper, blue	.50
2 ozs. magnesium ribbon	1.20
1 lb. magnesium chloride	.12
1 lb. manganese chloride	.50
2 lbs. manganese dioxide, powdered	.85
3 lbs. manganese dioxide, in lumps	1.00
5 lbs. mercury	4.00
¼ lb. mercuric chloride	.40
8 ozs. red oxide of mercury	.80
¼ lb. mercurous nitrate	.40
1 lb. nickel chloride	.70

1 oz. phenolphthalein	.10
5 lbs. paraffin	.75
1 oz. red phosphorous	.15
¼ lb. yellow phosphorous	.25
¼ oz. potassium	.45
1 lb. potassium bromide	.20
2 lbs. potassium hydroxide, sticks	.60
1 lb. potassium carbonate	.16
5 lbs. potassium chlorate, crystals	.70
1 lb. antimony and potassium tartrate	.60
2 lbs. potassium bichromate	.32
½ lb. potassium ferrocyanide	.30
½ lb. potassium ferricyanide	.30
½ lb. potassium iodide	2.40
1 lb. potassium nitrate	.15
¼ lb. potassium sulphocyanate	.15
3 lbs. potassium chloride	.25
½ lb. potassium permanganate	.10
1 oz.. platinized asbestos	5.00
½ oz. silver foil	.60
½ lb. silver nitrate	4.00
8 oz. sodium	.70
2 lbs. sodium carbonate crystals	.25
3 lbs. caustic soda, sticks	.75
2 lbs. sodium chloride, c. p	.50
¼ lb. sodium chlorate	.10
3 lbs. sodium nitrate	.42
2 lbs. sodium sulphate, crystals	.25
1 lb. sodium sulphide, crystals	.10
2 lbs. sodium hyposulphite	.15
1 lb. sodium phosphate	.10
2 lbs. sodium bisulphite	.60
½ lb. sodium acetate	.25
1 lb. sodium peroxide, commercial	.70
½ lb. stannous chloride	.25
1 oz. strontium chloride	.10
5 lbs. roll sulphur	.25
1 lb. flowers of sulphur	.08
3 lbs. granulated zinc	.45

3 lbs. zinc in sticks, at least 6 inches in length	.25
5 lbs. zinc in lumps or short, thick rods, 1 inch long, "for Kipps"	1.25
1 lb. zinc sulphate	.25
½ lb. zinc nitrate	.50
1 lb. granulated tin	.55
2 ozs. glass wool, fine	1.00

Cost of Supplies.

The prices given in the list of "Individual Supplies" are those that would be charged at Austin, hence they include freight.

The prices for the other supplies are to serve as *indications* merely; they have not been obtained by special quotation from a firm; and they do *not* include freight. For the latter about 10 to 15 per cent must be added to the price.

The total cost of the supplies in this list, figured for a teacher and twelve students, and including freight, is:

Individual sets	$135.00
General supplies	232.00
Freight and drayage, 12½ per cent on the latter	25.00
Total	$392.00

First Cost of Laboratory.

If all furniture is constructed as cheaply as possible, its cost will be approximately as follows:

12 lockers, for students, including plumbing	$100.00
Reagent side shelves, shelves in storeroom, work table for teacher, and large sink	50.00
One draft hood	25.00
Chemical supplies	392.00
Total	$567.00

Cost of Maintenance.

The least annual cost of maintenance is about $8.00 to $12.00 per student. Of this amount from $2.50 to $5.00 may be borne by the student, and the remainder by the Board. In many Texas high schools, the Board's appropriation is as much as $10.00 per student annually.

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CHEMISTRY IN THE HIGH SCHOOL

PARTS II AND III

BY

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PROFESSOR OF PHYSICAL CHEMISTRY
THE UNIVERSITY OF TEXAS

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list collects all necessary details for a number of the common oxy-acids, and these facts and relations should be learned by the student:

Name	Ion Formulae	Formulae of Anhydrides	Dualistic Formulae
Sulphurous acid	H_2SO_3	SO_2	H_2O,SO_2
Sulphuric acid	H_2SO_4	SO_3	H_2O,SO_3
Nitrous acid	HNO_2	N_2O_3	H_2O,N_2O_3
Nitric acid	HNO_3	N_2O_5	H_2O,N_2O_5
Phosphorous acid	H_3PO_3	P_2O_3	$3H_2O,P_2O_3$
Phosphoric acid	H_3PO_4	P_2O_5	$3H_2O,P_2O_5$
Carbonic acid	H_2CO_3	CO_2	H_2O,CO_2

NOTE.—Salts derived from sulphurous acid are called sulphites; from nitrous acid, nitrites, etc.

40. Nearly all the common acids are soluble in water, and hence their anhydrides hydrate on contact with water.

To demonstrate the hydration of acid oxides, drop a little phosphorus pentoxide into water.

41. Acid Salts.

Salts in which all the replaceable H's of the acid have been exchanged for metal "atoms" are called *normal* salts. It is possible, however, to exchange only a part of the H's in acids having more than an H in the molecule; since such salts still contain replaceable H's, and on this account exhibit *acid* properties, they are called *acid-salts*.

The formation of acid-salts takes place in the following manner: When an acid such as phosphoric, H_3PO_4, separates into its main constituent parts (ions), at first only one H separates, leaving the remainder intact as a monovalent ion $(H_2PO_4)'$; and when the first portions of a base are added to a solution of such an acid, the reaction of neutralization takes place as though H_3PO_4 were a monovalent acid, the composition of the acid radical of which is $(H_2PO_4)'$. Hence the aluminium salt would have the formula $Al(H_2PO_4)_3$.

NOTE.—The valence of *metals* and all positive ions is designated with an asterisk—e. g., H^*; that of acid radicals and other negative ions by an apostrophe, as NO_3', SO_4'', etc.

After enough base has been added to neutralize all of the first set of H-ions, then the second H ionizes extensively and leaves the bivalent ion $(HPO_4)''$; hence salts formed under these conditions appear to have a formula similar to those formed with bivalent acid ions, e. g., $Al_2(HPO_4)_3$.

After the second hydrogen has been neutralized, then the ten-

dency to ionize the third hydrogen may become effective, leaving the trivalent ion $(PO_4)'''$.

Of course if enough base is added all at once to neutralize more than one or two H's the reaction immediately proceeds to the corresponding extent. Thus if a drop of sulphuric acid is added to more than enough of sodium hydroxide solution to neutralize the acid completely, then the salt Na_2SO_4 is formed immediately; but when the procedure is reversed, that is, when a drop of sodium hydroxide solution is added to a great deal of sulphuric acid, then it will form only the acid salt $Na(HSO_4)$.

The (experimental) formation of acid salts, with polybasic acids, depends only on the relative proportions of acid and base mixed.

42. The following experiment is intended to demonstrate the formation of acid salts:

Secure a fresh solution of tartaric acid, $H_2(C_4H_4O_6)$, containing about 150 grams per liter, and a solution of potassium hydroxide containing about 200 grams to the liter and fill two burettes with these solutions, respectively. Measure out 10 cc. of potassium hydroxide solution into a small flask, add 15 cc. of the tartaric acid solution measured from the other burette, then heat the mixture to the boiling point, add a drop or two of phenolphthalein solution and finish neutralizing it by adding more tartaric acid from its burette. Cool the mixture under a jet of tap water and add to it as much tartaric acid again as was necessary to neutralize the potassium hydroxide. Crystals of potassium acid-tartrate will be formed, according to the equation—

$$K_2(C_4H_4O_6)+H_2(C_4H_4O_6)=2KH(C_4H_4O_6)$$

Next heat the mixture to boiling and add KOH slowly, with constant stirring until an amount approximately equal to the original amount has been added. Note that the crystals dissolve as KOH is added. Explain what happens in each step and write the equations of the three reactions. Note that the second portion of potassium hydroxide used is equal to the first portion used. The composition of the crystals that separated from the solution is $KH(C_4H_4O_6)$, and they are called: potassium acid-tartrate, or potassium bitartrate. Give reasons for both names.

43. 1. Figure out the formulae of the acid-sulphates or bisulphates of sodium,—of calcium,—of aluminium.

2. State whether or not it is theoretically possible to obtain acid salts of the following acids: Nitric acid, carbonic acid, acetic acid?

3. To distinguish the *three* different phosphates from each

other, we designate as primary phosphates those formed by replacing one *H;* as secondary, those formed by replacing two H's; and as tertiary those formed by replacing all three H's.

Write out the formulae of the three phosphates of calcium, and also the formulae of the two ferric sulphates.

CHAPTER VI.

IONIZATION AND THE GENERAL RELATION BETWEEN DISSOLVED ACIDS, BASES, AND SALTS WHICH RESULTS IN METATHETICAL REACTION.

44. Electrical Conductivity.

If a conducting wire in an electric circuit is cut and the wire ends thus produced are immersed into an aqueous solution of any acid, base, or salt, the electric current will flow again through the circuit,—which shows that such solutions are conductors of electricity. Although during the passage of the electric current through these solutions no visible change is produced except where the wire ends touch the solutions, yet the conducting is done by—or is due to—a certain special form of the substances present throughout the solution, and not to the changes which take place where the wire ends touch the liquid. The visible action at the wire ends does not necessarily involve the same substances as those involved in conducting the current through the solution. In this chapter the attention is to be directed to the substances that do the conducting through the solutions. The first experiments given below are intended to show upon what sorts of facts is based the belief that the conductivity of solutions is due to the presence of certain forms of the dissolved substance.

45. The circuit to be used in the following experiment is that passing through a 110-volts electric light (a sixteen-candle carbon lamp). In the absence of an electric light circuit a suitable magneto electric generator should be secured (see footnote). Cut one of the two wires leading to the electric light. To the two open ends thus obtained attach covered copper wires (annunciator wire) of such length that they will extend into a beaker on the desk where the work is to be conducted. The wire ends which are to be dipped into the solution should have the cotton cover removed for a length of at least one and one-half inches. With a 110-volt circuit passing through an incandescent light no particular precaution need be taken in handling these open ends except not to allow them to come in contact with gas pipes, water pipes or other direct connections with the ground.

When these ends are put into contact with different substances the lamp will light up with a brightness somewhat proportional to their conductivity, and with very poor conductors (so-called non-conductors) the lamps will not light up at all.

(NOTE.—The special *magneto generator* made by the Central Scientific Co. Catalogue, 1914, No. 2276 (price $5.00), has been found to be very suitable and very convenient in place of an electrical light circuit for this work.)

Try the conductivity of different substances: of a piece of wood, an iron nail, a lump of sugar, a mass of dry table salt, alcohol, distilled water, kerosene oil, etc.

For the purpose of comparing the conductivities of various solutions, a beaker of about 350 cc. capacity is to be filled half full with the various solutions prepared as stated below, and the bare ends of the copper wire from the electric circuit are to be held the same distance apart in all trials (e. g., near the wall on diametrically opposite sides), and immersed to the same depth (e. g., one-half inch). This is done in order to secure in every trial the same length and cross section of the conductor between wires.

Put distilled water into the beaker, try its conductivity, then add some soluble salt, for example, common salt; stir the mixture with a glass rod, and try the conductivity of the resulting solution: it conducts well. Compare the conductivity of this solution with the conductivity of its components—water and dry salt. Pour out the solution and remove the remnants of this solution by rinsing the beaker with a little distilled water.

The result obtained above might lead to the conclusion that the property of electrical conducting is produced by mere dissolution; to ascertain that mere dissolution does not change a substance from a non-conductor to a conductor, try in the same manner the conductivity of an aqueous solution of sugar.

The second trial indicates that not all dissolved substances are conductors. The question arises: will a substance like sodium chloride which dissolved in water forms a conducting solution,—will it form a conducting solution in *all* solvents? An indication for an answer to this question may be obtained by trying the conductivity of the same salt dissolved in 95 per cent alcohol. This solution conducts very poorly,—in fact, the conductivity of the alcohol is not appreciably increased by dissolving salt in it. Hence it appears that the salt dissolved in water must have undergone some other change besides mere dissolution, which change has converted the solution into an electrical conductor. The same is equally true of all acids, bases, and salts.

46. The State in which Acids, Bases, and Salts Exist in Aqueous Solutions.

A careful consideration of a large number of different experimental facts has led chemists to the conclusion that the particular change which occurs when acids, bases, and salt dissolve in water consists of the separating of some of the molecules into distincts parts called *ions*,—each of which carries a definite number of electric charges, the number of which is the same as the valence number of the ion. Metal ions and hydrogen ions carry positive charges, while the non-metals, the acid radicals, and the

hydroxyl (OH) ions carry negative charges. This "dissociation" takes place as follows: The metal atoms or the "acid" hydrogens give to the other parts with which they are associated in the molecules of acids, bases, and salts *as many* particles of negative electricity (called *electrons*) as their valence number amounts to. Thus when sodium chloride "ionizes," each Na gives *one* electron to the Cl from which it separates. The absence of this electron from the otherwise neutral Na is what is called a positive electric charge, and the presence of this electron on the Cl is what is called a negative electric charge. Every ion has on it as many electric charges as its valence number amounts to,—thus Cu has two positive charges, SO_4 has two negative charges, etc. The presence of these charges is expressed by various means—in this book a positive charge is denoted by an asterisk placed at the upper right-hand corner of the symbol, and the negative charge by an apostrophe placed as usual; e. g.: Cu^{**}, Cl', K^*, SO_4'', Al^{***} or Al^{3*}, PO_4''', or $PO_4^{3'}$, etc.

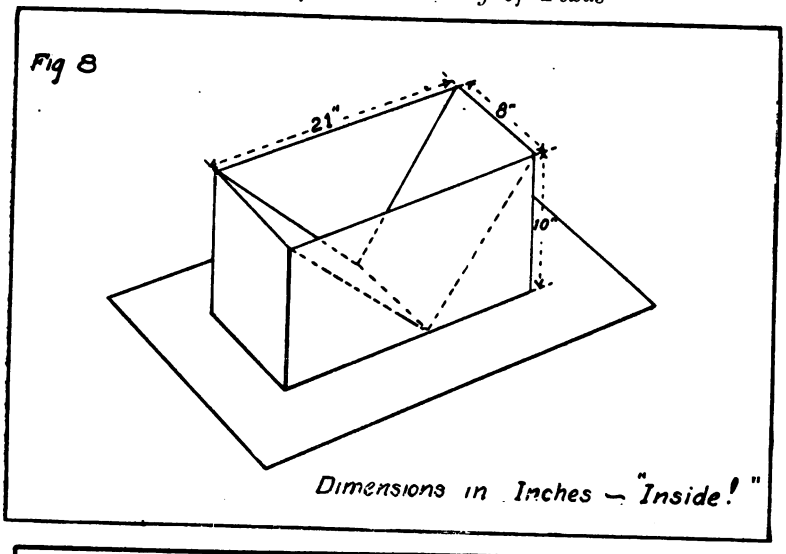
The conduction of the electric current through a solution takes place by the actual moving of the ions with their electric charges.

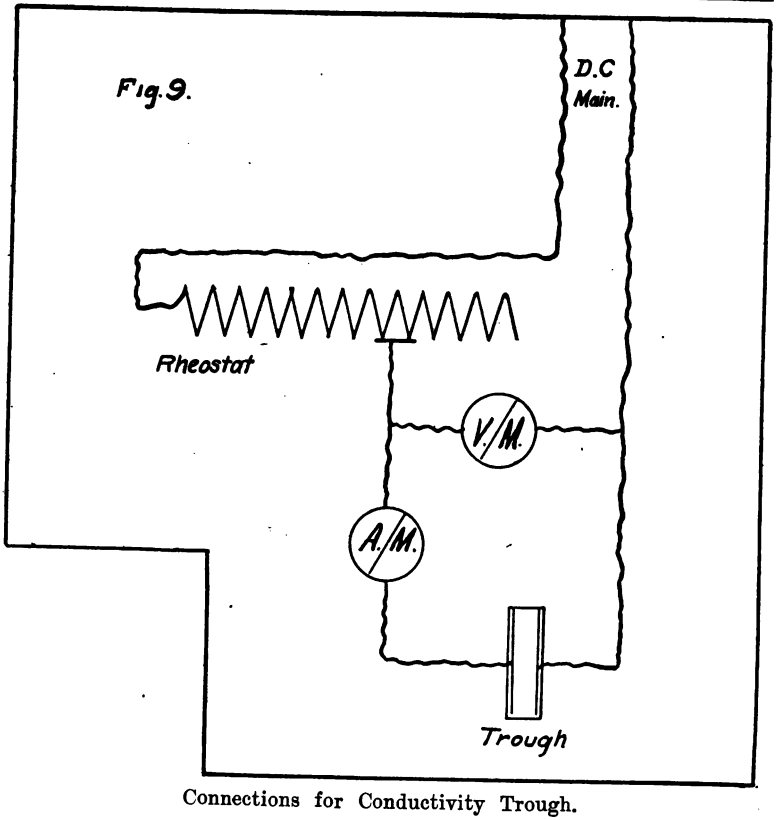
The composition of the ions was ascertained mainly by noting what parts of all acids, bases, and salts appear as displacing each other in forming new compounds. Thus it was observed that hydrogen is displaced by metals, OH is displaced by the various acid radicals, etc., and in the absence of any indications to the contrary it was concluded that these interchangeable parts are the distinct ions.

Not all of an acid, base, or salt in a solution is present in the form of ions: a part is present in the undissociated or combined part. This is due to the fact that the ions recombine when they meet. Thus it appears that there are two opposing actions possible in solutions of acids, bases, and salts,—ionization and recombination. These two opposing actions—or rather their tendencies to action—hold each other in equilibrium when a certain fraction of the dissolved substance is in the form of ions and the remainder in the undissociated form. With different substances these fractions of ions present in a solution have different values. In all solutions this ion fraction becomes larger on dilution until with extreme dilution *all* of the substance is in the form of ions.

47. Demonstration of the Increase of the Ion-Fraction with Dilution and the Determination of the Value of the Ion-Fraction of a Certain Solution.

Have a carpenter make a wooden vessel of the shape and dimensions given in the accompanying figure. Stout cypress or soft pine boards, at least 1¼ inches thick and perfectly smooth on both sides, are to be used. The vessel should be as nearly water





Connections for Conductivity Trough.

tight as the carpenter can make it. It should then be thoroughly covered on the inside with melted paraffin to make it absolutely water tight, and in order that the boards may not take up any of the solutions poured in it. Now secure from a plumber or cornice maker a piece of fairly stiff sheet copper, at least 16 inches square. Cut it from one corner diagonally across to the opposite corner into two triangular pieces. Trim each piece if necessary so that each sheet of copper may cover exactly one of the triangular ends of the trough. Bend over the excess of each plate at the top, and clamp or place each copper plate so that it may stick closely to the wooden end of the trough it covers. Provide any suitable means for connecting the copper sheets to the wires of an electric circuit. Shake up about 200 grams of crystals of copper nitrate with about 200 cc. of water until a *saturated solution* is obtained. By means of the apparatus used in the preceding experiment ascertain if this solution is a good conductor or not. Then take about 100 cc. of this solution and pour it into the trough. Secure an ammeter of the total capacity of about one ampere; secure a voltmeter with a capacity of about three volts; secure a source of direct electric current with a voltage of five to ten volts (e. g., 6-8 dry cells); and secure a sliding rheostat, "G. R." 10-15 ohms resistance and a carrying capacity of at least three amperes. Connect up the apparatus and the trough as shown in accompanying figure. Turn on the current and adjust with the rheostat until about 0.1-0.2 amps. are passing. Note accurately both ammeter and voltmeter readings which are then shown by the instruments. In the following operations adjust the current so that the *first* voltage between the poles *which has just been read* is kept constant, and record in parallel columns the amount of current that flows *after each* dilution of the solution. Dilute the solution by adding measured amounts of distilled water: at first in portions of 100 cc. at a time, subsequently in larger portions of several 100 cc. At the beginning, the increase in current will be relatively large with each addition of water; then it will become less until finally no further increase in current is obtained.

Divide the final (maximum) value into the first value (obtained with the original solution); this gives the fraction of the salt present as ions in the original solution.

Finally by means of the apparatus used in the preceding experiment compare the conductivity of the most dilute solutions here obtained with the conductivity of the original solution.

A little thought will reveal that the conductivity trials made in beakers are designed to compare the ease or difficulty with which the same amounts of different solutions conduct the electric current through the same distance; and the trough experiment is

designed to compare the ease or difficulty with which a constant amount of a salt in different volumes of water will conduct the electric current through a constant distance (i. e., the distance between the copper plates).

Since the ease with which a solution conducts the electric current through a certain distance depends upon the number of ions present between the poles, it follows from the above experiment that a certain amount of a salt dissolved in a large volume of water contains altogether more ions than when dissolved in a small amount of water. It should be noted, however, that a certain volume (say 1 cc.) of a dilute solution of a salt contains less ions than the same volume of a concentrated solution of this salt.

48. Ascertain the conductivities of the following: Dilute hydrochloric acid; dilute acetic acid; dilute sodium hydroxide solution; dilute ammonia solution; sodium acetate solution; ammonium chloride solution.

These experiments show that both acids and bases differ greatly in their "degrees of ionization" while salts show no notable differences even though they are derived from acids and bases which differ greatly in their degrees of ionization (which trial shows this point about salts?).

The following general statement covers the degrees of dissociation of all common substances. It should be committed to memory:

All normal salts, all strong acids (hydrochloric, nitric, sulphuric), all strong bases (that is, all *soluble* bases except ammonia) ionize extensively in aqueous solutions.

All weak acids (acetic, carbonic, sulphurous, phosphoric), all weak bases (ammonia) and water itself, are very slightly dissociated (about 1 per cent and less) in aqueous solutions.

It should be noted here that insoluble or slightly soluble substances produce or maintain only few ions in solution.

The chemical activity of acids, bases, and salts is not proportional to their total concentration, but is proportional to the concentration of their free ions. This general fact is strikingly illustrated by the great difference in the rate of action, upon zinc, of the strong acids (hydrochloric acid, dilute sulphuric acid) as compared with the slow rate of action of weak acids (acetic acid, phosphoric acid). Test tube trials of these actions should be made if the facts cannot be recalled readily by the students.

49. Details of the Relations Between Dissolved Substances Which Undergo Metathetical Reactions.

Extensive study of the reactions between acids, bases, and salts has led to the following conclusions:

1. Anions and cations combine readily to form neutral mole-

cules and in any solution every possible combination of the anions with the cations present is formed.

2. The amount of any one combination formed depends upon the tendency of this combination to ionize: If it has a great tendency to ionize, then the amount actually formed from the ions is naturally small even if, to begin with, the solution contains many free ions of this combination; if the combination to be formed has a slight tendency to ionize, the amount of this combination formed *may* be great.

To illustrate the above: When a solution of an acid (HCl) has a solution of a base (NaOH) added to it, then the two cations (H* and Na*) will, on meeting the anions (Cl' and OH') form the four combinations,—HCl, NaCl, NaOH, HOH. Of the first three compounds only small amounts can be formed because their tendencies to ionize are so great that small concentrations of these substances are enough to stop further combining. But the fourth substance has such a slight tendency to ionize that it does not prevent the uniting of its ions until the supply of either H* or OH' ions is practically exhausted.

It appears from the above that the only extensive change in this solution is the disappearance of the H* and OH' ions which form water according to equation: $H^* + OH' = H_2O$.

50. The disappearance of these two ions can be demonstrated by a conductivity trial. For this purpose dilute some sodium hydroxide solution until its conductivity is so slight that the lamp in a circuit will burn dimly. Dilute some hydrochloric acid to the same extent. Then add a drop of phenolphthalein solution to the sodium hydroxide and neutralize it with the acid solution: ascertain the conductivity of the neutral mixture. It will be found to be much less than that of the two components. If no ions had disappeared the mixture would have shown the same conductivity as the solutions from which it was prepared. The lesser conductivity indicates a decrease of ions and thus accords with the explanation of the reaction given above.

The equation for the above reaction is commonly written as follows:

$$NaOH + HCl = NaCl + HOH$$

In this equation the change appears as a simple transposition (metathesis) of each anion from one cation to the other, hence such reactions are called metathetical reactions.

In order to express the fact that metathetical reactions between acids, bases, and salts consist of the extensive formation of a new combination of ions in a solution, it is necessary to write the symbols of the substances in some way so as to indicate whether they are present mainly in the form of free ions or mainly in the non-

ionized form. This is accomplished by marking the symbols of the ionized substances with the signs which indicate the electric charges; while the undissociated substances are written as usual. The equation for the action in the above equation should hence be written as follows:

$$Na^*OH' + H^*Cl' = NaCl' + H_2O.$$

Although a solution of any salt mixed with the solution of any other salt, acid, or base would produce at least small amounts of two new compounds (e. g., $Na^*Cl' + K^*NO_3' = K^*Cl' + Na^*NO_3'$), yet such slight formations of new compounds are not ordinarily noticeable and hence are not considered to be reactions. Only the extensive formation of a combination of ions is spoken of as a reaction.

51. The Fundamental Relation Which Brings About Metathetical Reactions.

It is evident from the foregoing that a metathetical reaction will take place whenever one of the two new ion combinations possible in a mixture of solutions has a much smaller tendency to ionize than the tendency with which the corresponding free ions tend to combine. Briefly and definitely, this condition which brings about a metathetical reaction is expressed as follows for the reaction under consideration above:

$$\begin{matrix}[H^*]\times[OH'] \\ \text{in original} \\ \text{mixture}\end{matrix} \quad > \quad \begin{matrix}[H^*]\times[OH'] \\ \text{from pure} \\ \text{water}\end{matrix}$$

This means that the *product* of the concentrations of the H^* and OH' ions as found in the original mixture just before reaction is greater than the product of the concentrations of these ions as found in pure water. The concentration or amount per 1 cc. of a substance is indicated by placing square brackets around its chemical symbol. The *product* of the concentrations of the combining ions (shown in the left-hand expression) measures their tendency to combine; while the expression on the right is a measure of the tendency of water to form ions. Evidently the extensive combining of the H ions from HCl and the OH ions from NaOH can take place only when the tendency indicated by the left-hand expression is greater than that indicated by the right-hand expression. It should be noted that it is necessary to take the *product* of the two ion concentrations in order to obtain a measure of their reacting tendency. It was shown before that the reacting tendency of a single substance is proportional to its concentration alone; but when two substances act together their combined ten-

dency to reaction is proportional to the product of their concentration. This is a universal fact and one of great importance.

The fundamental relation which brings about metathetical reactions is now to be illustrated with a number of other examples: since the ideas involved in all of them are the same as those presented above, these illustrations all appear under the same heading.

52. If a solution of sodium acetate is mixed with a solution of hydrochloric acid, the accidental meetings of the ions would form the two new combinations *acetic acid* and *sodium chloride.*

What is the extent of ionization of each of the four combinations in the mixture? Hence does the contents of the original mixture show the relation which is necessary to cause metathetical reaction? In other words, is either one of the following relations true?

1. $[Na^*]\times[Cl']$ in original mixture $>$ $[Na^*]\times[Cl']$ from its own solution

2. $[H^*]\times[C_2H_3O_2']$ from original mixture $>$ $[H^*]\times[C_2H_3O_2']$ from its own solution

Evidently one of them is true, hence the reaction takes place. The free hydrogen and acetions combine mostly to undissociated acetic acid molecules. This lessening of the ions in the mixture may be demonstrated by means of conductivity experiments. For this purpose, dilute some hydrochloric acid until its conductivity is so slight that it allows the lamp to burn but dimly. Dilute a solution of sodium acetate to the same extent. Mix equal volumes of these solutions and try the conductivity of the mixture.

The equation for this metathetical reaction is

$$H^*Cl+Na^*C_2H_3O_2'=Na^*Cl'+HC_2H_3O_2$$

The only change that takes place in this mixture is the combination of the hydrogen ions and the acetions to form undissociated acetic acid.

53. Proceed as in the preceding example but use any strong base as sodium hydroxide in place of hydrochloric acid and the solution of a salt of a weak base, ammonium chloride, in place of sodium acetate.

In the foregoing examples the conductivities of the resulting mixtures are less than those of the components. This is not a necessary condition as may be seen from the following example.

54. Secure some weak base, dilute ammonium hydroxide, and some dilute weak acid, acetic acid, and test their conductivities:

both of them conduct so poorly that the lamp will show only a dim glow. Mix equal volumes of these solutions, and try the conductivity of the mixture.

As all metathetical reactions, so this reaction takes place because a new combination of ions can be formed extensively. The relation which shows exactly why reaction takes place is the following:

$$\begin{matrix}[H^*]\times[OH'] \\ \text{in original} \\ \text{mixture}\end{matrix} \quad > \quad \begin{matrix}[H^*]\times[OH'] \\ \text{from pure} \\ \text{water}\end{matrix}$$

It appears that although there are only few hydrogen ions and few hydroxyl ions present, and hence their combining tendency is correspondingly slight, yet the combination, H_2O exerts such a slight ionizing tendency that it does not effectively oppose the combining of the hydrogen and hydroxyl ions. As the hydrogen ions disappear the equilibrium between the undissociated acetic acid and its ions is destroyed so that more of the acetic acid can ionize. The acetate ions remain free and accumulate. At the same time the disappearance of the hydroxyl ions allows the further ionization of the undissociated ammonium hydroxide to take place. The greater conductivity shown by the resulting solution is due to the accumulated acetate and ammonium ions.

55. Dilute a solution of silver nitrate until its conductivity is so small that the lamp will glow dimly. Secure two or more of the following chlorides and prepare similarly dilute solutions of them:—sodium chloride, potassium chloride, ammonium chloride, calcium chloride, magnesium chloride. Then mix equal volumes of a chloride and of silver nitrate solutions; note the separation of white silver chloride from the mixture and try its conductivity. The latter will be found to be perceptibly less than that of either constituent.

In this reaction nearly all of the undissociated silver chloride formed separates from the solution as soon as it is formed because it is practically insoluble. Evidently the small amount of undissociated silver chloride which remains in solution cannot form many ions or cannot exert a great ionizing tendency, hence the following relation may be expected to hold:

$$\begin{matrix}[Ag^*]\times[Cl'] \\ \text{in original} \\ \text{mixture}\end{matrix} \quad > \quad \begin{matrix}[Ag^*]\times[Cl'] \\ \text{in saturated} \\ \text{AgCl solution}\end{matrix}$$

Since this action really involves the silver and chloride ions only and since the chloride ions from all chlorides are identical it might have been expected beforehand that all the chlorides mentioned above would react in the same way.

56. Repeat the preceding experiment in every detail, using barium chloride in place of silver nitrate and two or more of the following sulphates in place of the chloride above: sodium sulphate, potassium sulphate, ammonium sulphate, copper sulphate, and magnesium sulphate. Recall to mind the solubilities and degrees of ionization of these substances and of the new ones which could be formed by a different combination of the ions in the mixtures, ascertain from this data whether metathetical reaction could take place in these mixtures, and state the particular relation on account of which reaction takes place.

57. State whether or no a metathetical reaction will take place when solutions of the following pairs of substances are mixed, and point out which ion pair fulfills the fundamental condition that brings about the reaction:

1. Sodium carbonate and sulphuric acid.
2. Potassium sulphite and hydrochloric acid.
3. Sodium carbonate and calcium chloride.
4. Sodium chloride and acetic acid.
5. Sodium chloride and copper sulphate.
6. Sodium phosphate and copper nitrate.

58. In the foregoing examples the differences in solubilities and in degrees of ionization between the substances in a solution mixture are so large that a *general* knowledge of solubilities and degrees of ionization of salts, acids, and bases suffices to estimate in a sense whether or no the necessary conditions exist for the ensuing of metathetical reactions. However, when the differences in solubilities and in degrees of ionization between substances in a solution mixture are very small, then the above statement of solubilities and of degrees of ionization do not enable one to foretell whether or no a reaction would take place. The following experiment presents such a case.

59. Test the conductivity of the distilled water at hand; then add some powdered calcium phosphate to the water, stir the mixture and try its conductivity:—the lamp will glow dimly. Calcium phosphate is ordinarily said to be insoluble, but the fact that the water has become a conductor shows that an appreciable amount of this salt has dissolved and ionized. Let the mixture remain at rest long enough to allow most of the undissolved salts to settle to the bottom, then pour the nearly clarified liquid into another beaker. In the meanwhile dilute some hydrochloric acid to such an extent that its conductivity will be the same as that of the calcium phosphate solution. Mix equal volumes of this acid and of the clarified solution of calcium phosphate and ascertain the conductivity of the mixture; it will be perceptibly less than that of its component.

Evidently the *dissolved* calcium phosphate and the acid have reacted: the reason for this may be readily seen from a consideration of the degrees of ionization of the four possible combinations in the mixture. State the relation which has brought about the reaction. The occurrence of this reaction could evidently have not been foreseen from the general statements concerning solubilities and degrees of ionization of substances.

60. Put a small amount of calcium phosphate into a beaker, cover it with a small quantity of water, and while stirring the mixture add small portions of dilute hydrochloric acid until all of the solid has dissolved.

Since the liquid medium in this last experiment is essentially nothing but water, and since water dissolves only a small amount of calcium phosphate, the question arises: how does the hydrochloric acid aid the dissolution of this salt? The answer is indicated partly by the result of the conductivity trials above and for the sake of clearness the action will be assumed to take place in stages, as follows: (1) calcium phosphate dissolves until the solution is saturated; then (2) the dissolved calcium phosphate reacts with the hydrochloric acid, as a result of which the dissolved calcium phosphate disappears; then (3) the liquid dissolves more calcium phosphate and this cycle of actions begins over again. These are the details of the action which takes place whenever any insoluble substance is dissolved by means of an acid, base, or salt, and these details should be learned and retained by the student.

CHAPTER VII.

CARBON, SULPHUR, NITROGEN, THE HALOGENS AND RELATED COMPOUNDS.

Text-book reading will be assigned on the subjects of this chapter, and in this connection the following experiments are to be performed.

61. Difference Between Charcoal and Graphite.

Place a porcelain crucible on a clay covered triangle, tilting it so that it rests on its side. Put a small piece of charcoal into the crucible and heat it with a burner to ascertain how readily it burns. Then try a piece of graphite in the same manner. Although these two substances are chemically identical, yet they show themselves to be physically quite different. This is generally true of *allotropic* forms of a substance.

62. The Role of Certain Gaseous Compounds of Carbon in Metallurgy—Reduction of Oxides of Metal.

Secure a piece or a stick of charcoal, and boil it in a concentrated solution of sodium carbonate. This treatment renders it practically non-combustible and the stick will thus serve as a suitable holder for the metal oxide.

Close the air holes of a Bunsen burner, and turn down the flame to one-third its usual height. Moisten the end of the charcoal stick and dip it into some powdered lead oxide, then hold it in the center of the flame:—globules of metallic lead will appear immediately.

63. The Preparation of Carbon Dioxide, and the Demonstration of Some of its Common Properties.

Fit up a 500 cc. flask with a two-hole rubber stopper, a dropping funnel, and a delivery tube made by bending an ordinary glass tube, twelve inches long, near its mid-point to a right angle. Put into the flask a handful of powdered sodium carbonate (commercial washing soda). Moisten the salt with water and when ready to collect the gas, allow dilute sulphuric acid to drip into the flask from the dropping funnel. The following reactions take place with this mixture:

$$Na_2{*}CO_3'' + H_2{*}SO_4'' = Na_2{*}SO_4'' + H_2CO_3$$
$$H_2CO_3 = H_2O + CO_2$$

By means of a piece of glass tubing pass the gas through a little distilled water in a test tube until the water is saturated

(to determine the latter, close the test tube with the thumb, shake it vigorously, and note whether or no a partial vacuum is created in the tube). Does the gas appear to be very soluble? Try blue litmus paper on this solution: What ions must be present to produce this change of color? Show by an equation how they were produced.

64. Relation Between the Components of a Carbon Dioxide Solution.

A glance at the equations above and at the last equation written reveals the fact that in the last trial carbon dioxide and water combine, while in the preparation of carbon dioxide they separate. Evidently this change is reversible; as in all such actions, so in this, equilibrium is attained when the concentrations of the substances on the two sides of the equations bear a certain ratio to each other. If the relative concentration of H_2CO_3 is greater than this ratio then it breaks up into CO_2+H_2O; and if its relative concentration is less than this ratio, then CO_2 and H_2O combine.

Every aqueous solution of carbon dioxide has in addition to the equilibrium just pointed out, another equilibrium—namely, between the gas CO_2 and the dissolved CO_2: the gas dissolves in water or is liberated from the water until the concentration of the CO_2 gas above the water bears a certain ratio to the dissolved CO_2.

Hence a saturated aqueous solution of carbon dioxide presents the following equilibria:

1. CO_2 gas$=CO_2$ dissolved.
2. CO_2 dissolved$+H_2O=H_2CO_3$ undissociated.
3. H_2CO_3 undissociated$=2H^*+CO_3''$.

In connection with the last equilibrium it should be mentioned that all polybasic acids, such as H_2CO_3, H_2SO_4, H_3PO_4, ionize the *second* H^* ion with a much smaller tendency (to a much smaller extent) than the first. and a third H^* ion to a still smaller extent. It is on this account that such acids form *acid salts*: with the first set of H ions such acids act as stronger acids than with the second set.

Place a small piece of burning candle at the bottom of a large beaker and allow carbon dioxide to flow into the beaker until the flame is extinguished.

Pass carbon dioxide downward into a dry, wide-mouth bottle (500 cc.) while keeping the mouth of the bottle covered as well as possible with a piece of glass. Fasten some magnesium ribbon to the end of a piece of iron wire, ignite it, and lower it into the bottle: then try to find the carbon produced. Write the probable equation of this reaction. The burning of the magnesium in this gas is due to the high temperature created by the large amount

of heat evolved from this reaction: at very high temperatures carbon dioxide dissociates (into oxygen and CO, or into oxygen and carbon) and thus oxygen becomes available for the continuation of the combustion.

Put about 50 cc. of clear lime water into a small conical flask, allow carbon dioxide to pass into this solution until the precipitate first formed is redissolved, and then boil the solution. Ascertain from your text what changes have taken place, learn the equations and note where these changes take place in nature and in daily life.

65. The Fundamental Relation which Brings about Metathetical Reactions in the Preparation of Carbon Dioxide.

The fundamental relation on account of which sodium carbonate solution and dilute sulphuric acid react is evidently—

$$\begin{matrix}[H^*]\times[CO_3''] \\ \text{in original} \\ \text{mixture}\end{matrix} \quad > \quad \begin{matrix}[H^*]\times[CO_3''] \\ \text{from saturated} \\ \text{solution of } H_2CO_3\end{matrix}$$

The expression on the right is small *first* because the solubility of carbonic acid is small, and second, because this small amount of carbonic acid is only slightly ionized. It is hence not surprising that all carbonates—even so-called insoluble carbonates—react when mixed with any, even weak, acids. Hence in general it may be said that carbon dioxide may be prepared by taking any carbonate and treating it with any acid.

Make test tube trials with several different acids and carbonates to demonstrate the above statement. Write all equations. In practice, sulphuric acid would not be used with calcium carbonate—why?

66. a. An Illustration of a Commercial Source of Sulphur.

Heat a little iron pyrite in a test tube to show that it gives up free sulphur, just as manganese dioxide gives up free oxygen when heated: $3FeS_2 = Fe_3S_4 + 2S$.

b. Some Physical Properties of Sulphur.

Bend a test tube slightly at the mid points, and put some sulphur into it; melt this and distil it, allowing it to drop into some water,—merely to show that it can be melted or distilled.

c. The Combination of Sulphur With Metals.

Mix some fine iron filings with an equal bulk of sulphur, put the mixture into a test tube, and start it to reacting by heating the lower end of the tube until the glow started there proceeds

practically of its own accord up through the mass. Write equation of reaction. Show that a new substance has been formed: for this purpose add hydrochloric acid to small amounts of the original and of the resulting substances, and note any differences in the behavior of these mixtures.

67. a. The Preparation of Sulphur Dioxide and the Demonstration of Some of Its Properties.

Prepare sulphur dioxide from a "mush" of bisulphite of soda and concentrated sulphuric acid, using the same apparatus as for carbon dioxide. Equations of reactions?

b. The Oxidation of Sulphur Dioxide by the Oxygen of the Air.

Saturate 100 cc. of water in a flask with the gas obtained in a. Test the solution with litmus. Test a few drops of it by adding first a few drops of hydrochloric acid and then a few drops of barium chloride solution. Since barium sulphite is soluble in water, should there be any reaction? Put 20 cc. of the same solution into a medium-sized flask and shake it vigorously so as to bring it extensively into contact with the oxygen of the air. Test again with hydrochloric acid and barium chloride. Note difference from b and explain giving all equations.

c. The Oxidation of Sulphur Dioxide by Means of Oxidizers.

Take another portion of the solution above and add to it potassium permanganate solution, a drop at a time, until no further change occurs. The color change shows that the permanganate is reduced,—that it gives up oxygen. Oxydize still another portion of the solution with a little concentrated nitric acid and note the brown fumes formed; these indicate that the nitric acid has been reduced. Test the resulting mixtures with barium chloride solution.

d. Bleaching Action of Sulphur Dioxide.

Moisten some flowers and expose them to the sulphur dioxide in a flask: note that the color disappears.

State briefly the properties of sulphur dioxide which have thus been shown experimentally.

68. 1. Point out the fundamental relation which brings about metathetical reaction in the preparation of sulphur dioxide by the method prescribed above.

2. When sulphur dioxide is absorbed in water, the same reaction takes place as with carbon dioxide:—write out the equations for the equilibria in this solution.

3. Write in *proper order* the equations for the reactions that take place when sulphur dioxide is absorbed in an excess of sodium

hydroxide. If sulphur dioxide is added to the mixture *after* the sodium hydroxide has been neutralized, what reaction will take place then?

69. The Preparation of Ammonia and an Illustration of its Solubility.

In order to secure several liters of ammonia gas conveniently, heat some concentrated ammonia solution in a flask fitted with a two-hole rubber stopper, through which pass a safety tube and a conducting tube, and dry the gas by passing it through a cylinder filled with quick lime. Fill an inverted stout bottle with the gas by upward (why?) displacement of air (why not water?). Fix the bottle with a stopper and a glass nozzle pointing inward and dip the outer end into a basin of water to which phenolphthalein has been added. Result?

70. Some Properties of Ammonia and Ammonium Salts.

Try the effect of litmus on ammonia water; add hydrochloric acid to some aqueous ammonia until litmus paper indicates that the base has been utilized. Evaporate the mixture to dryness in a dish, then heat the dry salt until it has volatilized completely; compare this behavior of the ammonium salt with the behavior of salts of metals such as potassium, sodium, etc.

Put a few drops of concentrated aqueous ammonia in a dish and hold a rod which has been dipped into concentrated hydrochloric acid over it. What is formed? Equation.

71. The Fundamental Relation Which Brings About the Metathetical Reactions Between Ammonium Salts and Strong Bases.

Put some dry ammonium chloride into each of two test tubes; do the same with ammonium sulphate; add to one portion of ammonium chloride and to one portion of ammonium sulphate a little sodium hydroxide solution, and to the other portions some slaked lime and a few drops of water. Warm the mixtures and note the evolution of ammonia. Equations?

72. 1. Point out the fundamental relation which brings about a metathetical reaction between any ammonium salt and any strong base.

2. What equilibria are present in an aqueous solution of ammonia?

3. Write in proper order the equations for the reactions that take place when ammonia gas is absorbed in dilute sulphuric acid.

73. The Fundamental Relation Which Brings About the Metathetical Reactions in the Liberation of Hydrochloric Acid Gas From Chlorides.

Prepare some hydrochloric acid gas by adding concentrated sulphuric acid to test tubes containing sodium chloride, ammonium

chloride, and magnesium chloride, respectively. Try also the effect of concentrated phosphoric acid and of concentrated acetic acid, respectively, on sodium chloride. The formation of hydrochloric acid gas may be revealed by holding a glass rod with a few drops of aqueous ammonia on it near the mouths of these test tubes. These substances, which react here to produce hydrochloric acid gas, do not react when they are dissolved in water. Hence, what is likely to be the condition, due to the absence of water, which brings about the metathetical reaction that produces hydrochloric acid gas?

74. The Preparation and Collection of a Bottle Full of Hydrochloric Acid Gas.

Secure the same flask and fittings used for the generation of carbon dioxide and of sulphur dioxide; put into the flask 25 c.c. of concentrated hydrochloric acid, and allow concentrated sulphuric acid to drop into the flask through the dropping funnel. Collect the gas by downward displacement of air in a dry bottle. Show the solubility of this gas as you showed the solubility of ammonia.

75. The Preparation of Chlorine.

The reactions involved in the preparation of chlorine involve entirely different fundamental facts than the metathetical reactions studied at present, hence the preparation of chlorine does really not fit in here. However, it is desirable to demonstrate here the properties of the element and hence its preparation must be given. The details of the reactions involved in the preparation of chlorine are not to be considered here and the general fact alone is to be learned that oxidizing agents react with hydrochloric acid to give water and free chlorine. The oxidizing agents may be considered to be suppliers of oxygen merely and the oxygen they supply reacts with the hydrochloric acid according to the following equation:

$$O+2HCl=H_2O+2Cl$$

This is the only equation to be learned here in connection with the preparation of chlorine.

The following test tube trials are intended to show that any strong oxidizing agent will liberate chlorine from hydrochloric acid. Note that most of the oxidizing agents used below can be used to prepare oxygen—which indicates that they have a great tendency to give oxygen.

Put into separate test tubes a pinch of each of the following substances: manganese dioxide, lead dioxide, potassium chlorate, potassium nitrate, potassium permanganate. Add a few drops of concentrated hydrochloric acid upon each one of these powders,

and hold the test tubes up to the light to see the greenish yellow gas generated by the mixture. Do not inhale the gas! It is likely to produce nausea and inflammation of the lining of the throat.

76. a. The Preparation and Some of the Properties of Chlorine.

Prepare several liters of chlorine gas by allowing a concentrated solution of calcium permanganate to drop upon concentrated hydrochloric acid in a flask fitted with a dropping funnel and a delivery tube. Collect two wide-mouth bottles full by downward displacement of air.

b. Its Reactivity.

Dip a little cotton into hot turpentine and thrust the cotton into a bottle full of chlorine. Result? Into another bottle sprinkle a little powdered antimony. Result? Expose some moist colored calico to chlorine gas from ten to fifteen minutes. Result?

77. The Action of Hydrofluoric Acid on Glass.

Cover a piece of glass with melted paraffin. Scratch through this paraffin cover, making any figure you please, and pour aqueous hydrofluoric acid upon the scratches and allow it to remain there for fifteen minutes or more. (Do not get any hydrofluoric acid on the skin, because it produces painful, slowly healing sores.) Remove the paraffin with gasoline and note that the glass has been etched. Note in what kind of bottles hydrofluoric acid is kept. Look up the equation for the reaction between silica and hydrofluoric acid. Silica is one of the chief components of glass and is the one which is attacked by the acid.

The Preparation of Hydrofluoric Acid.

Mix a little calcium fluoride and concentrated sulphuric acid in a test tube. Warm the mixture and allow the gas evolved to act on the sides of the test tube for fifteen minutes or more. Wash out the test-tube, allow it to dry, and then examine it(?). Note the similarity between the preparation of this gas and that of hydrochloric acid gas, and hence make your conclusions as to the conditions that bring about the metathetical reaction between calcium fluoride and concentrated sulphuric acid.

78. The Preparation of Hydrobromic and Hydriodic Acid Gases by Metathetical Reaction and the Liberation of the Non-Metals From Them.

Put some potassium bromide crystals into a test-tube, cover them with concentrated phosphoric acid, and warm the mixture: to reveal the hydrobromic acid gas formed, dip a glass rod into

some ammonia and bring it near the mouth of the test-tube. Then try, in the same way, potassium iodide with concentrated phosphoric acid. Compare these reactions of the bromide and iodide with the reaction that a chloride would give. Add a pinch of manganese dioxide to the contents of each of these test-tubes and warm the mixture. What is obtained now? What would have been obtained with chlorides?

79. A Demonstration of the Mutual Replacing Power of the Halogens.

To a solution of potassium bromide add some chloroform and some chlorine water; the latter will form bromine by reaction. Shake the mixture; the chloroform collects the bromine because the latter is more soluble in chloroform than in water. Repeat the whole, using potassium iodide in place of potassium bromide. Finally treat some potassium iodide solution with bromine water and chloroform.

In these reactions the free element present at first displaces the combined element. This power of displacement is in the order: chlorine, bromine, iodine. This should be remembered. The equations for the reactions are very simple, e. g.: $KBr+Cl=KCl+Br$. Write the others.

CHAPTER VIII.

THE ACTIONS AND USES OF GENERAL REAGENTS FOR SOLUTIONS OF SALTS.

80. There are some substances which react with salts of many metals and which are employed to produce desired combinations of ions or to establish the presence or absence of various metal ions in solutions: such substances are called general reagents. Although a general knowledge of the solubilities and degrees of ionization of these reagents and of the various compounds of the metals enables one to foresee many of the reactions that could take place between them, yet there are some reactions which cannot be foreseen because they involve a more accurate knowledge of solubilities and degrees of ionization or of still other special facts. Some of this more accurate knowledge of solubilities, of degrees of ionization, and of other special facts forms an essential part of chemical information, and is therefore given in this chapter.

In the selection of the facts, experiments and exercises of this chapter, the salts of the following metals were carefully considered:—salts of other metals are assumed to be absent: Ag^{*}, Hg^{*}, Hg^{**}, Cd^{**}, Pb^{**}, Cu^{**}, Bi^{***}, Al^{***}, Fe^{***}, Fe^{**}, Ni^{**}, Zn^{**}, Mn^{**}, Ca^{**}, Sr^{**}, Ba^{**}, Mg^{**}, K^{*}, Na^{*}, NH_4^{*}.

81. Sodium (or Potassium) Hydroxide as a Reagent.

Secure solutions of water soluble salts of the following cations: Cu, Ag, Zn, Cd, Hg (ous), Hg (ic), Pb, Fe (ous), Fe (ic), Ni, Al, Mg, Ca.

To a few cubic centimeters of each of these solutions in a test-tube add a few drops of sodium hydroxide solution, shake each mixture and note its appearance; then add a few drops more of the reagent, and so continue until the reagent has been added in a relatively large amount, say, about twice as much reagent by volume as of salt solution, if the two solutions are of approximately equivalent concentrations. Compare the results with the statements in the table below.

General Facts.—By strict metathetical reaction the *hydroxides* should be obtained in the mixtures below. However, in many cases the substances finally obtained are not the hydroxides of the metals but substances derived from them through one or both of the two following changes:

(a) Dehydration,—complete ($Hg(OH)_2$ to HgO) or partial ($Cu(OH)_2$ to $Cu_2O_2(OH)_2$).

(b) Dissolution of the precipitated hydroxide by excess of the reagent, thus showing that the precipitated hydroxide func-

tionates as an acid, e. g. $Zn(OH)_2$ dissolves in excess of NaOH solution as per equation:

$$H_2ZnO_2 + NaOH = Na_2ZnO_2 + 2H_2O.$$

The formula for zinc hydroxide is thus written to *suggest its functionating as an acid.*

RESULTS OF ACTION OF SODIUM (OR POTASSIUM) HYDROXIDE UPON AQUEOUS SOLUTIONS OF SALTS OF THE COMMON METALS.

Ba—$Ba(OH)_2$ is precipitated only from concentrated solutions because it is soluble in 20 parts of water—white.

Sr—Ppt. $Sr(OH)_2$ sol. in 60 parts of H_2O—white—not precipitated from dilute solutions.

Ca—Ppt. $Ca(OH)_2$ sol. in 700 parts H_2O—white—not precipitated from *very dilute* solutions.

Mg—Ppt. $Mg(OH)_2$ sol. in 6000 parts H_2O—white.

Al—Ppt. $Al(OH)_3$ white, sol. in excess of reagent, giving $NaAlO_2$.

Zn—Ppt. $Zn(OH)_2$ white, sol. in excess—Na_2ZnO_2.

Pb—Ppt. $Pb(OH)_2$ white, sol. in excess—Na_2PbO_2.

Ferrous—$Fe(OH)_2$ white ppt., darkens on exposure to air (oxidizes).

Ferric—$Fe(OH)_3$ reddish brown, flocculent ppt.

Mn—Ppt. $Mn(OH)_2$—"flesh" colored, darkens on exposure to air.

Ni—Ppt. $Ni(OH)_2$—pale green.

Cu—in cold solution, $Cu(OH)_2$—bluish white ppt., soluble in large excess of reagent; in hot solution, CuO—black ppt.

Cd—$Cd(OH)_2$, white ppt.

Bi—$Bi(OH)_3$, white ppt.

Ag—Ppt. Ag_2O—greyish brown.

Hg (ous)—Ppt. Hg_2O—black.

Hg (ic)—Ppt. HgO—yellow—in order to avoid the formation of differently colored basic salts, the Hg salt solution must be poured *into* the reagent.

Exercise (a) In what way can it be readily ascertained whether or not a substance has been completely precipitated, say, $Fe(OH)_3$ by NaOH? Hence would sodium hyroxide be employed as a precipitant for aluminium if it be required that precipitation be complete? From the metals given in the table above select those for which sodium hydroxide may thus be used as a precipitant.

(b) Required: to change the copper in copper nitrate completely to pure copper chloride. This cannot be done simply by adding hydrochloric acid to copper nitrate solution because the con-

ditions in such a mixture would not bring about the required metathetical reaction except to a very slight extent, and it would be physically impossible to extract all the copper as pure copper chloride from this mixture. However, this conversion can be easily accomplished by the intermediate precipitation of copper oxide by means of sodium hydroxide,—as follows:

Heat the copper nitrate solution to the boiling point, and then add to it, drop by drop, sodium hydroxide solution until the disappearance of the blue color shows that all the copper ion has left the solution. When the copper oxide has settled, decant the supernatant liquid as completely as possible, add a small amount of hot water to the residue, stir the mixture, allow the solid to settle, and decant this liquid. This "washing" of the solid may be repeated. Then add to the copper oxide just enough dilute hydrochloric acid to dissolve the oxide, and evaporate the solution partly until it deposits crystals on cooling.

This method is capable of general application: thus the magnesium in magnesium chloride might be changed completely to magnesium nitrate by the same method.

(c) State what will happen when *an excess* of sodium hydroxide is added to a solution which contains both aluminium and ferric salts? Try this operation, using the least excess necessary; then dilute the solution in order that it may not attack filter paper,—then filter it: note that you have thus separated the aluminium from the iron. This method is capable of general application: thus, cadmium and zinc may be separated in the same manner.

AMMONIA AS A REAGENT.

82. Since a solution of ammonia contains OH' ions, it might be expected to be similar in its action to a solution of sodium hydroxide. However, it differs from the latter in several respects: it is a *weak* base while sodium hydroxide is a strong base; the cation of ammonium hydroxide (NH_4) is composed of several atoms, while that of sodium hydroxide is composed of one atom; and a solution of ammonia contains not only ammonium hyroxide and its ions, but also a great deal of ammonia in the form of NH_3. Hence it is not surprising to find that ammonia is capable of many special reactions. These are presented briefly in the following list:

A. Solutions of salts of Ag, Cu, Cd, Zn, and Ni react with excess of ammonia to form solutions of complex metal-ammonia salts, in which the cations have the composition:

$Ag(NH_3)_2$*, $Cu(NH_3)_4$**, $Cd(NH_3)_4$**, $Zn(NH_3)_4$**, $Ni(NH_3)_4$**.

Very few free metal-ions (Ag*, Cu**, etc.) are present in these solutions, hence the following relation holds for them—

$$[Cu^{**}]\times[OH'] \text{ in this mixture} < [Cu^{**}]\times[OH'] \text{ in plain solution of this combination}$$

therefore ammonia reacts with and dissolves the hydroxides of these metals.

Secure in test tubes very small amounts of solutions of salts of copper, zinc, and nickel: add to each, first, a small quantity of ammonia, which may produce precipitates, and then add more ammonia until after stirring the mixtures clear solutions are obtained. Note the color change which occurs with copper and nickel salts: this color change is indicative of the formation of the new compounds.

B. Solutions of salts of magnesium and manganese react slightly with ammonia to form precipitates of their hydroxides; but as soon as this reaction has produced enough ammonium salt (how?) or if enough of an ammonium salt has been added before adding the ammonia to the mixture then no action takes place. While precipitation takes place the solution presents this relation—

$$[Mg^{**}]\times[OH'] \text{ in original mixture} > [Mg^{**}]\times[OH'] \text{ in a plain solution of this combination}$$

but afterwards the reverse relation exists. This difference is due to the fact that plain ammonia contains more OH' ions than its mixture with an ammonium salt. The ammonium salt decreases the OH' ions in such a mixture in a manner explained below.

To demonstrate the foregoing, add ammonia to one portion of the magnesium salt solution; and to the other portion add, first, ammonium chloride and then ammonia.

A Demonstration of the Suppression by Ammonium Salts of the Free OH' Ion in Ammonia.

This demonstration depends upon the fact that phenolphthalein has a pink color in solutions containing enough OH' ions, but that it is colorless in solutions containing none or an insufficient concentration of OH' ions.

Take two beakers, put into each one some ammonia and a drop of phenolphthalein and dilute the mixture with water until its color is a pale pink. Then add to one some solid ammonium chloride, and to the other any other solid ammonium salt and stir the mixtures: they will become colorless.

As has been stated before, the combining tendency of an ion pair is proportional to the product of its concentration—e. g., $[NH_4^*]\times[OH']$. When the solution is undisturbed, this combining tendency is in an equilibrium with the ionizing tendency of the undissociated portion (in this example, NH_4OH). But when an ammonium salt is added to the solution the concentration of the NH_4^* ions is increased enormously, hence the product $[NH_4^*]\times[OH']$ becomes momentarily too large for this equilibrium and some of the ions combine to lessen the values of NH_4^* and OH' until equilibrium is again attained with the ionizing tendency of the undissociated ammonium hydroxide. This *decrease* reduces the small amount of OH' ions so much that the concentration of the remainder does not affect phenolphthalein.

C. Solutions of salts of Ca, Sr, Ba do not react with ammonia because they would form strong bases, and such mixtures present the relation—

$$\begin{matrix}[Ca^{**}]\times[OH'] \\ \text{in mixture}\end{matrix} \quad < \quad \begin{matrix}[Ca^{**}]\times[OH'] \\ \text{in saturated} \\ \text{solution of this} \\ \text{combination}\end{matrix}$$

D. Solutions of salts of Hg and Pb react with ammonia to form precipitates:—e. g., $HgCl_2$ forms NH_2HgCl,—$PbCl_2$ forms $Pb(OH)Cl$.

E. Solutions of salts of the tri-valent metals Bi, Al, Fe, react with ammonia to form precipitates of their hydroxides—under all conditions.

83. Rule for the Practical Use of Ammonia.

1. In using ammonia as a reagent, always have an ammonium salt (e. g., NH_4Cl) present in the mixture before adding the ammonia.

2. In the absence of Hg and Pb salts this ammonia mixture will give precipitates with the tri-valent metal ions only and none with any other metal ions. This working rule is the only part of the above that should be definitely remembered.

84. By the use of ammonia, separate bismuth from a solution containing bismuth and copper salts; Al from a solution containing Al and Ni salts; Fe (ic) from a solution containing ferric and Mg salts.

Give directions for changing the aluminium in potash alum completely to aluminium chloride.

HYDROGEN SULPHIDE AS A REAGENT.

NOTE.—Hydrogen sulphide is poisonous, hence generators of this gas should be used either outside of the building or in hoods in which there is a strong draft.

85. Preliminary Consideration.

Hydrogen sulphide is a weak acid:—in its aqueous solution it is only slightly ionized into $2H^*$ and S''. When the concentration of the H^* ions in an aqueous solution of hydrogen sulphide is increased (e. g., by adding HCl), the concentration of the S'' ions becomes less for the same reason for which the concentration of the OH' ions in ammonia becomes less when the concentration of the NH_4^* ion is increased.

86. General Facts.

The sulphides of the alkali metals and of the alkaline earth metals (Na, K, NH_4, Ca, Sr, Ba, Mg) are soluble in water; hence hydrogen sulphide does not react with solutions of salts of these metals. It does not react with salts of Al, because Al_2S_3 is decomposed by water.

All other sulphides are insoluble; hence hydrogen sulphide reacts with the neutral (or alkaline) solutions of salts of all metals except the above,—but in the presence of many H^* ions (acidified solutions), hydrogen sulphide reacts only with the salts of Cu, Hg, Pb, Ag, Bi, and Cd, and it does not react, in acidified solutions, with the salts of Zn, Fe, Ni, Mn. Commit this fact to memory.

This difference is due to the fact that the small concentration of S'' ions in acidified solutions is large enough to give with salts of Cu, Bi, etc., the relation—

$$[Cu^{**}]\times[S''] \text{ in original mixture} \;>\; [Cu^{**}]\times[S''] \text{ in a plain saturated solution of CuS}$$

while with salts of Zn, Mn, etc., the relation is—

$$[Zn^{**}]\times[S''] \text{ in the mixture} \;<\; [Zn^{**}]\times[S''] \text{ in a sat. sol. of ZnS}$$

However, in neutral or alkaline solutions, the S'' ion concentration is greater than in acidified solutions, and the relation in such a solution is—

$$[Zn^{**}]\times[S''] \text{ in original mixture} \;>\; [Zn^{**}]\times[S''] \text{ in a plain sat. sol. of ZnS}$$

Hence under these conditions the reaction takes place.

87. Colors of Precipitated Sulphides.

The colors of sulphides are a valuable means for identifying the metals. Freshly precipitated sulphides have the following colors:

FeS, NiS, Ag_2S, HgS, PbS, Bi_2S_3—dull black.

CuS—brownish black.

ZnS—white (when pure!).

CdS—Yellow.

MnS—pink or flesh color.

NOTE.—During precipitation, HgS frequently exhibits several other colors—black, yellow, red—but with excess of H_2S it finally becomes black.

88. Reactivities of Precipitated Sulphides.

For further operations on the metal ions which have been converted to insoluble sulphides, it is necessary to know what reagents will act on them and produce soluble salts. This knowledge may also be used as a means of identifying the metal ions.

The reagents under (b) and (c) below will also react upon the sulphides in the groups above their own; but the reagents of (a) and (b) *do not* react upon the sulphides in the groups below them. In all cases the metals dissolve because they are changed to water soluble salts.

(a) Sulphides which react metathetically with dilute HCl or dilute H_2SO_4:—

ZnS, FeS, MnS, CdS.

CdS requires a stronger "dilute" HCl than the others.

(b) Sulphides which react with dilute HNO_3—action complex, resulting in free sulphur and nitrates of metals:—

Ag_2S, PbS, CuS, Bi_2S_3, NiS, CoS.

(c) HgS reacts with free chlorine: for this purpose the HgS is covered with a small amount of concentrated HCl; the mixture is warmed slightly and a few very small crystals of potassium chlorate are dropped into it.

89. Demonstration of the Use of the Foregoing Facts in the Separation of Metal Ions and Their Conversion to Desired Compounds.

The following three exercises require considerable care in their performance:

Put 10 to 20 cc. of dilute copper sulphate solution and an equal amount of zinc sulphate solution in a small flask, add 10 to 20 drops of dilute HCl, heat to boiling, treat with H_2S in excess and filter. What is the substance on the filter paper? The reaction

that has taken place is metathetical—write the equation. What is the by-product? Evidently the concentration of the hydrogen ion has been increased during the progress of the reaction. Since with *excessive* concentration of hydrogen ion, hydrogen sulphide is unable to precipitate any sulphides, and since it is possible that in this experiment the concentration of the acid has become excessive, the last portion of copper may not be precipitable under the conditions. Hence a small part of the solution must be diluted largely by adding an equal volume or more of water, or the acid may be partially neutralized by the cautious addition of a base. Then it should be heated again and treated with hydrogen sulphide. If necessary, treat the main portion of the solution in this way and repeat this procedure until precipitation is complete.

Before proceeding to precipitate the zinc sulphide, it is desirable to remove the remnant of hydrogen sulphide which remains dissolved in the liquid, since otherwise it starts precipitation as soon as the acid is neutralized by ammonia or any other base. To remove this gas, boil the liquid well for two or three minutes.

Then add ammonia to the clear (and odorless) solution until it is plainly alkaline. If enough ammonium salt is present (from what source?), then no precipitate will be formed. Next, treat the solution with hydrogen sulphide again. A *white* precipitate (ZnS) will be formed (a trace of iron compounds introduced by the hydrogen sulphide may impart a "dirty" color to the precipitate). Filter and wash the precipitate.

The ammonia added above performs *two* functions: first, it neutralizes the free acid present, and second, it forms ammonium sulphide with the hydrogen sulphide. Write the metathetical reaction of the action of ammonium sulphide *with the zinc salt.*

With the aid of a porcelain spoon transfer the CuS to a dish, add a little dilute HNO_3, and warm the mixture. A solution of $Cu(NO_3)_2$ will be obtained by complex reaction. Note the free sulphur formed.

Drip dilute HCl slowly upon the ZnS on its filter paper until all has been dissolved and collected in a beaker placed below. The reaction is metathetical (*?*). Note the evolution of H_2S.

Using this separation of copper from zinc as a model, precipitate separately as sulphides the metals from a solution containing any one of the following pairs of metals—cadmium and nickel, bismuth and manganese. Continue the treatment for the precipitation of the first metal until the second sulphide can be obtained *pure*—as shown by its color. Wash the cadmium or bismuth sulphide with distilled water while it is on the filter paper (to remove remnants of the salt of the second metal), and convert it to the nitrate. Convert the nickel or manganese to the chloride.

90. The following questions refer to any one of the three mixtures worked in the preceding experiments:

1. If a magnesium salt is also present in one of these mixtures, what becomes of the Mg^{**} ions during the course of the procedure?
2. If silver salts are also present in the above mixtures, what would happen at the beginning of the procedure? What would be the best method to remove the Ag^{*} ion so as not to interfere with the rest of the procedure as given?
3. If aluminium salts are also present in any of these mixtures, what would happen in the course of the procedure and how could the Al^{***} ions be removed without interfering with the rest of the procedure?
4. What other metal ions, if present, would have shown the same behavior as Ag in question 2 above?
5. What other metal ions, if present, would have shown the same behavior as copper, cadmium, or bismuth in the experiments above?
6. What other metal ions would have shown the same behavior as Al in question 3 above?
7. What other metal ions would have shown the same behavior as zinc, nickel or manganese in the experiment above?
8. What other metal ions would have shown the same behavior as magnesium in question 1 above?

91. Take a mixture of solutions of zinc and nickel salts, precipitate the sulphides of these metals together under suitable conditions (?), gather them on a filter, transfer the mixture to a beaker with the aid of a porcelain spoon, add dilute hydrochloric acid to the mixture and stir it (reaction?). Gather the residue on another filter, wash it with water (?), then put it into a dish (if necessary, put into the dish also the filter paper to which the substance clings) and convert this residue into a soluble salt (how?).

92. Optional Exercise.

Secure a mixture of solutions of cadmium and mercuric salt, precipitate the sulphides together, collect them on a filter, transfer them to a dish with the aid of a porcelain spoon, add dilute nitric acid, and warm and stir the mixture. Then dilute it with water and filter it, wash the residue, transfer it to a dish (if necessary put into the dish also the filter paper to which the substance clings) and convert it to a soluble salt by means of the proper solvent. State in detail all that has happened.

SPECIAL TESTS FOR SOME METAL IONS.

93. These tests need not be definitely remembered because they may be looked up when needed. However, the student should try every one of them with known substances to become acquainted with these experimental facts.

1. AgCl is soluble in ammonia, from which solution AgCl may be reobtained by neutralizing the ammonia with an acid (HNO_3).

2. $PbCl_2$ is very soluble in *hot* water, though not in cold water.

3. HgCl forms a black compound with ammonia, for which the formula and reaction need not be learned.

4. $HgCl_2$ is reduced to HgCl or Hg by $SnCl_2$ solution, the latter becoming $SnCl_4$.

5. When a drop of bismuth salt solution is added to a beaker full of water, a white cloudy precipitate will be obtained: Bi*** ion can exist in solution only if many H* ions are present; but if the concentration of the H* ion is reduced sufficiently by dilution, then the bismuth ion reacts with water (hydrolizes) according to the following equations:—

$$Bi^{***}Cl_3' + 3HOH = Bi(OH)_3 + 3H^*Cl'$$
$$\text{or } Bi^{***}Cl_3' + H_2O = BiOCl + 2H^*Cl'$$

None of the other metal ions considered in this chapter have this property.

6. Note that the following salts and their solutions are colored:—

Copper salts—blue or green.
Nickel salts—blue or green.
Ferrous salts—pale green.
Ferric salts—reddish yellow.
Manganous salts—pale amethyst.

7. Compounds of the following metals will color the Bunsen flame. To try this use a *clean* platinum wire, dip it into a solution of one of these metals and hold the drop of the solution in the flame:—

Bright red—Sr.
Brick red—Ca.
Yellow—Na.
Yellowish green—Ba.
Green to blue—Cu.
Blue, pale—Pb.
Violet—K.

8. Ammonia in compounds is revealed by treating them with a strong base (e. g., NaOH solution), warming the mixture, and noting the odor.

9. Since green or blue solutions contain either copper or nickel salts, it is desirable to ascertain by a direct test which of these two is present. For this purpose put granulated zinc into the solution:—this removes copper from the solution in accordance with the following equation—

$$Zn + Cu^{**}SO_4'' = Zn^{**}SO_4'' + Cu$$

10. To test for Mg^{**} ion, take a portion of the original solution and add—

(a) NH_4Cl solution: filter and discard any ppt. formed.
(b) NH_4OH solution: filter and discard any ppt. formed.
(c) H_2S: filter and discard any ppt. formed.
(d) Ammonium carbonate solution: discard any ppt. formed.
(e) Sodium phosphate solution: if a dense crystalline precipitate is obtained, it is $MgNH_4PO_4$.

Operations 1-4 are for the purpose of removing all metals except Mg, K, Na and NH_4. All other metals must be removed; they also form insoluble phosphates.

94. Exercise in Identifying Metal Ions.

Students will be given solutions that contain one or more metal ions: the problem for them is to identify, by means of the facts given in this chapter, the metal ions present in such solutions.

In this work it will be advisable to proceed somewhat as follows:

(1) Note the color of solution.
(2) Ascertain what color—if any—it imparts to the Bunsen flame.
(3) Test a small portion for ammonia.
(4) Test another small portion by adding (a) a few drops of dilute HCl: if no ppt. appears, add (b) H_2S: if no ppt. appears, boil to expel H_2S, and then add (c) NH_4OH till mixture is alkaline:—if no ppt. appears, add (d) H_2S.

When a precipitate is obtained in the foregoing, secure this precipitate from a large portion of the original mixture, collect it on a filter and wash it. Preserve this precipitate. Take a small portion of the filtered liquid, and *continue* with tests *4a* to *4d*:—if another precipitate is thus formed, secure this from the whole of the filtered liquid and collect on another filter. If necessary repeat once more the procedure given in the last sentence.

5. Any precipitates obtained in 4 should be examined as follows:

(a) Note their appearance.
(b) Precipitates obtained with HCl should have Special Tests Nos. 1-3 made on them.
(c) All other precipitates should be dissolved by suitable (?) means, and tested with NaOH solution or Special Tests Nos. 4-9.

6. Test for Mg^{**}—see Special Test No. 10.

CHAPTER IX.

FUELS AND INDUSTRIAL WATERS.

95. Fuels.

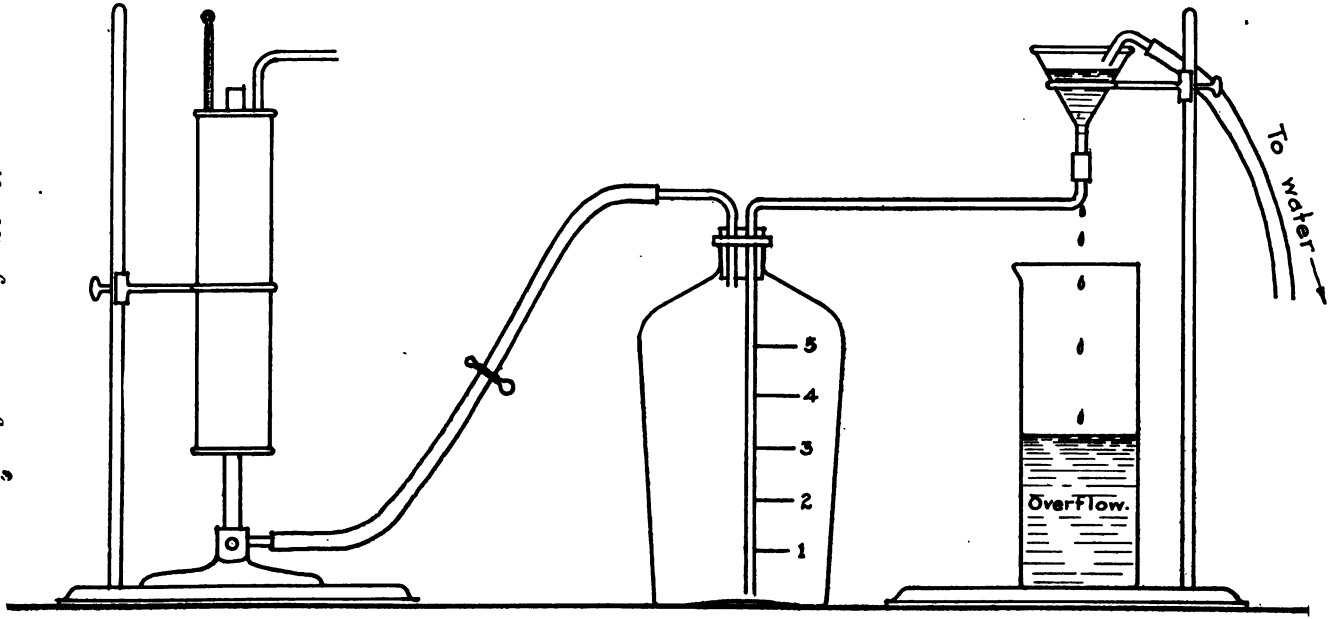
The value of a fuel depends, *first,* on the amount of heat which the combustion of a certain fuel furnishes; *second,* on the ease or difficulty with which it is handled. The second factor is not in the province of chemistry, but the first requires the chemist's aid.

The best way of determining the heating power of fuel is by direct measurement. The following examples show how this may be done by means of an inexpensive apparatus and with a fair degree of accuracy.

96. The Determination of the Heating Power of Fuel Gas with Graefe's Gas Calorimeter.

The special apparatus needed is the calorimeter vessel, the gas holder, and a special thermometer calibrated to .1° C. Wind several layers of wrapping paper (or better, of thin asbestos paper) loosely around the calorimeter vessel, and tie it around the bottom, middle and top. Fill the vessel with a definite quantity of water—e. g., one liter—at room temperature. Keep the wrapping dry. Suspend a thermometer into the vessel from a suitable support so that its bulb will be about half way down in the vessel. Fill the gas holder first with water, then replace most of the water with gas. Connect a burner with the gas holder and put a screw clamp on the rubber tube leading to the burner, by means of which the flame can be regulated. Assure yourself that a set of five or more copper gauze discs has been placed in the "chimney tube" of the calorimeter vessel; these gauze discs serve to conduct the heat of the burnt gases to the water chamber. Note carefully the initial temperature of the calorimeter. Turn on the water so that the funnel on the gas holder will overflow slightly even when the gas is being drawn. Close the air holes on the burner, turn on and light the gas and adjust its flow so that a flame one inch high is obtained. When the water level in the bottle has risen up to one of the calibration marks, put the burner under the calorimeter vessel and keep it there until two liters of the gas have been burned. Stir the water gently but steadily, and after shutting off the gas continue to stir until the thermometer thread begins to drop; note carefully the highest point reached by the thread.

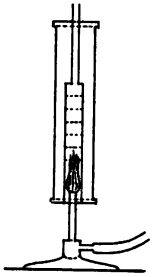
The next thing to do is to ascertain how much heat raises the temperature of this calorimeter through the same range of temperature in the same length of time,—in other words, we must calibrate the calorimeter. To do this, empty the warm water,



Dr. Graefe's Calorimeter for Gases.

Graefe's Calorimeter in Operation.

allow the calorimeter to regain the room temperature and weigh it to the nearest whole gram. Then add about 900 grams of water (at room temperature) and ascertain the weight of the whole. Then heat about 200 cc. of water to the boiling point and keep it boiling while adding small amounts of it to the calorimeter at such a rate that the temperature of the calorimeter will rise about as fast as it did when heated by the burner. When a temperature has been reached which is near the former observed final temperature, then the vessel and contents are weighed again to the nearest gram. The difference in this weight and the preceding weight gives the number of grams of water at 100° C. which have been added. This much water has been cooled down to the final tem-



Section of Calorimeter Vessel.

perature. Let us assume the latter to be 26° C., and let the amount added be 105 cc.:—then 105 (100-26)=7770 is the number of calories of heat added. This has raised the temperature of the calorimeter metal and 900 cc. through, say, 7° C. Then the amount of heat required to raise these only 1° is 1110 cals., and since 100 grams more of water would require another 100 cals. the total heat required per 1° C. is 1210 cals. This would be the calorific value of the calorimeter.

The calorific power of one liter of the fuel gas is then obtained by multiplying the observed rise obtained with one liter of the gas by the calorific value of the calorimeter.

97. To convert this result from calories per liter to British thermal units (B. T. U.'s) per cubic foot of gas multiply the above result by 142.5.

98. For convenience, the following definitions are here given: one small calorie is the amount of heat required to heat 1 gram of water through 1° C. (from 15° to 16° C.).

One B. T. U. is the amount of heat required to heat one pound of water through 1° F. (from 50° to 51° F.).

99. In spite of all precautions the escaping gases in the calorimeter experiment have a higher temperature than the calorimeter itself, hence they produce a heat loss which cannot be ascertained except by burning the same gas in this calorimeter and in another more elaborate instrument (e. g., a Junker's calorimeter) and comparing the results. However, this heat loss does not seriously affect our result.

100. The operation of a coal calorimeter is a little more troublesome than that of a gas calorimeter, hence no attempt is made here to use it. The fundamental idea in its use, however, is the same as that in the calorimeter above.

101. In commerce the value of a coal is frequently also judged from an examination of the coal such as is given below. This examination also reveals other useful facts about a coal, namely: How much gas could be made from it? How much coke? How much water will it lose on drying? These determinations constitute what is known as the proximate analysis of coal and they are made as follows.

102. The Proximate Analysis of Coal and Lignite.

A *proximate* analysis is a resolution of a substance into its *first* direct components.

(a) *Moisture.*—Crush the sample, weigh out accurately in a very small dish 1 to 2 grams of it, and place this in an air bath at approximately 105° C. for about one hour. Weigh again and calculate the per cent of loss in weight.

(b) *Volatile Combustible Matter.*—Secure a crucible with a well-fitting lid; weigh out, accurately, in it about 1 gram of the above dried sample. Place the crucible on a clay-covered triangle and heat it as strongly as possible with a good Bunsen burner. The heating is to be continued until gases *just* cease to be formed—which is usually in about five to eight minutes. Weigh and calculate the per cent of loss.

(c) *Fixed Carbon.*—Replace the above crucible and contents on the triangle, uncovered, and tilt it to one side. Heat it moderately and turn it so that all the carbon may be burned. Do the same with the lid, keeping the latter inverted while heating it. Replace the lid on the crucible and weigh the whole. The remainder *in* the crucible is *ash*. The difference between the last weight and the preceding is *fixed carbon.*

(d) *Ash.*—The remainder in the crucible, as already stated, is the ash. Express all in per cents.

103. Texas coals and lignites show the following limits of variations in composition:

Coal.

	From	To	Average
Moisture	3.46	13.44	7.40
Volatile and combustible matter	29.17	48.84	34.82
Fixed carbon	36.37	49.17	41.74
Ash	9.07	24.76	16.04
Sulphur	1.28	4.76	2.19
Heating power, British thermal units	9,609	12,264	11,245

Lignites.

	From	To	Average
Moisture	7.30	37.26	25.17
Volatile and combustible matter	20.33	45.62	37.59
Fixed carbon	21.09	38.92	28.45
Ash	4.81	16.11	8.79
Sulphur	0.41	0.96	0.65
Heating power, British thermal units	6,291	10,411	7,661

Compared with coals from Alabama, Pennsylvania, and Oklahoma, Texas coals are *low* in fixed carbon, high in ash and sulphur, and about the same in volatile and combustible matter. The coals from the States first mentioned have about 15 per cent more fixed carbon, but only half as much ash and sulphur as Texas coals. It is probably on account of this difference in composition that the Texas coals cannot be "coked."

Try to ascertain by inquiry what your local dealers and their patrons know about the coal in use in your neighborhood, and whether or no coal is bought and sold on its intrinsic value.

104. Industrial Waters.

With reference to their use in daily life, waters may be classified as follows:

(a) Potable waters—for domestic use.
(b) Industrial water—for use in boilers, in laundrying, etc.
(c) Irrigation waters.
(d) Mineral waters.

A water suitable for one purpose may be unfit for another, hence when a water is to be examined (*analyzed*—as it is called) it should be examined with reference to the use to which it is to be put.

105. When and How to Have Waters Analyzed.

Water for drinking purpose and general domestic use should be examined by a bacteriologist if there is any danger of the waters having been in contact with refuse from human habitations. If

it is free from "possible" bacterial contamination, and clear, odorless and palatable, it is fit for use irrespective of the salts it may contain.

Boiler waters which produce considerable incrustation on the walls of boilers, etc., should be examined for the amount of temporary and permanent *hardness*—as it is called. The determinations of temporary and permanent hardness are fairly simple and they are given below as an exercise.

Irrigation waters, unless practically free from salts, should be examined for the total amount of soluble salts they contain and for the presence of any sodium carbonate in them. The latter is particularly harmful to vegetation.

Mineral waters are important only on account of the salts they contain. Their analysis requires the service of an experienced chemist, and entails much labor—hence much expense. Mineral waters are rarely good business ventures; the salts contained in most of them are of common occurrence, and since these waters owe their whole value to the salts they contain, they are seldom worth the work of a special analysis.

Mineral waters should not be taken except upon the advice of physicians. The indiscriminate use of "sulphur" waters (which contain hydrogen sulphide) is especially to be warned against.

106. The Analysis of Boiler Waters and of Irrigation Waters.

On boiler waters, determinations are to be made of the amounts of total solids, temporary hardness and permanent hardness. On irrigation waters, determinations are to be made of the amounts of total solids, temporary hardness and of sodium carbonate; the total solids minus the temporary hardness gives the total soluble salts or total alkali, and the amount of sodium carbonate is the amount of black alkali in irrigation waters.

107. Test for Presence or Absence of Hardness and Black Alkali.

Test the water with both blue and red litmus paper:

(a) If it turns litmus *blue,* then the water probably contains sodium carbonate and is soft, i. e., it contains none of the salts which cause hardness.

(b) If it is neutral to litmus or turns litmus *red,* then sodium carbonate is absent and the water contains salts that produce hardness.

108. Total Solids Dissolved in the Water.

This determination is one of the most important to be made on a water, because it gives the sum of the amounts of the different solids determined by various other means.

Weigh a small size porcelain evaporating dish as accurately as possible. Measure out 250 c.c. of any water to be examined (which, if necessary, should have been previously filtered to remove sediment) and evaporate this gradually in the weighed evaporating dish over an asbestos board (adding the water in small portions at a time). Weigh the dish plus residue. Multiply the weight in grams by four to obtain the weight per liter, and then by 585.18 to obtain the number of grains per U. S. gallon of total solids in this water. Report also in parts per hundred thousand.

109. Determination of Temporary Hardness in Waters.

Amount of Calcium Carbonate in Solution (Present as Bicarbonate).—Place 100 c.c. of the water in a beaker. Add a few drops of methyl orange and then titrate with 1-50 normal sulphuric acid until the indicator shows neutrality (a piece of white paper placed under the beaker will sharpen the color change). Every c.c. of acid used up denotes the presence of one part of calcium carbonate in 100,000 parts of water. To express the result in grains per gallon, multiply this number of c.c. by 585.18.

This quantitative relation between the acid and the calcium carbonate is established as follows: A liter of *normal* sulphuric acid contains as much acid by weight in one liter as corresponds to one gram of hydrogen,—hence $\frac{1}{2}H_2SO_4$ grams, or 49 grams of sulphuric acid per liter. Since $1H_2SO_4$ reacts with $1CaCO_3$, the amount of acid in one liter of normal solution reacts with $\frac{1}{2}CaCO_3$ grams,—which is 50 grams. Hence one liter of a 1-50 normal acid reacts with *1 gram* of calcium carbonate and 1 c.c. reacts with .001 gram of calcium carbonate. Since the sample of water taken is 100 c.c. (which is the same as 100 grams of water), every 1 c.c. of acid used up indicates the presence of .001 parts by weight of calcium carbonate in 100 parts of weight of water, or 1 whole part of calcium carbonate in 100,000 parts of water.

110. Total Soluble Salts in Waters—Total Alkali in Irrigation Waters.

Subtract the amount of calcium carbonate from the amount of total solids found above: the remainder is the amount of "soluble salts" present in the water, in contradistinction to the calcium carbonate which is only soluble through free carbon dioxide and not by itself. The amount of soluble salts is also the "total alkali" in irrigation waters.

111. Amount of Black Alkali in Irrigation Waters.

Waters which turn litmus blue are to be titrated as though they are titrated for temporary hardness:—in this case the sulphuric acid is used up by the sodium carbonate present. The number of c.c. of 1-50 normal sulphuric acid multiplied by 1.22 gives the

number of parts by weight of sodium carbonate per 100,000 parts by weight of water. The factor *1.22* results from the relation of the molecular weights.—$CaCO_3$: Na_2CO_3 : : 100 : 122.

112. Permanent Hardness: Chlorides and Sulphates of Calcium and Magnesium.

Measure 100 c.c. of the water into a clean evaporating dish and add from a burette any definite amount of 1-50 normal sodium carbonate solution, and after stirring the mixture try a drop of it on litmus paper: it should turn litmus blue—otherwise more of the sodium carbonate solution must be added. Keep account of the total amount added. Evaporate the solution nearly or quite to dryness,—in a dish over an asbestos board. Add a little boiling water to the residue and filter the mixture, carefully avoiding any possible loss of drops of liquid by proper use of the stirring rod (instruction). Rinse the dish and the filter paper twice with small quantities of water and titrate it with the 1-50 normal sulphuric acid.

The sodium carbonate reacts with all the calcium and magnesium salts except with the calcium carbonate (present as bicarbonate). The sulphuric acid used was required by the *excess* of sodium carbonate used,—hence the difference between the total sodium carbonate and the sulphuric acid is the sodium carbonate required by the calcium and the magnesium present in the form of chlorides, sulphates, etc., i. e., the salts which cause permanent hardness.

Since normal solutions are so related in strength that 1 c.c. of one reacts with 1 c.c. of another it follows that if the number of c.c. of 1-50 normal sulphuric acid used above is greater than the number of c.c. of 1-50 normal sodium carbonate previously added, then the water itself contains some sodium carbonate and is naturally free from permanent hardness. In general it is then also free from temporary hardness and the sulphuric acid used up as in the determination of temporary hardness is used up by the sodium carbonate naturally present in such waters.

The number of c.c. of 1-50 normal sodium carbonate used is reported as the permanent hardness in "parts per 100,000 parts of water." Since the permanent hardness is due, in general, to four different salts with different formula weights ($CaCl_2$=112, $CaSO_4$=136, $MgCl_2$=95, $MgSO_4$=120), the weight of the salts which constitutes permanent hardness is not given by this report: the report gives the weight of an amount of calcium carbonate which would take the place molecule for molecule of the four salts above.

113. Alkali in Soils.

The soluble salts present in soils have the same effect on vegetation as the salts in the water poured upon the land; hence in

examining irrigation waters, the soil upon which they are to be used should also be examined.

For this purpose weigh out on a balance, suitable for weighing such large quantities, 200 grams of an air-dried representative sample of the soil to be examined (how would you secure a sample which is a fair representative or average of all different portions of the soil to be examined?). Pour upon this sample one liter of distilled water carefully measured: stir the mixture thoroughly at the beginning and also at intervals of ten to fifteen minutes, and after about two hours filter about 500 c.c. of the liquid and put this extract into a well stoppered bottle.

Analyze it just as you would an irrigation water, but report the results in parts per 100,000 parts *of soil.*

DATA ON THE INFLUENCE OF SOLUBLE SALTS (ALKALI) IN SOILS.

Sodium carbonate in soils and irrigation waters is much more objectionable than other soluble salts. It is known as black alkali because it brings about the extensive dissolution in water of the black soil humus.

The following table, prepared by the Bureau of Soils of the United States Department of Agriculture, shows the effect of different concentrations of alkali in soils, to a depth of six feet (in parts per 100,000):

Soil Grades	Total Salts in Soils	Black Alkali	Crop Behavior
Grade 1	0–200	Less than 50	Common crops not injured unless salt is concentrated in first foot.
Grade 2	200–400	50–100	All crops will grow except those most sensitive, but at the higher limit all except truly resistant are distressed. Alfalfa grows, but hard to get a good stand. Sugar cane, sorghum, and barley do well.
Grade 3	400–600	100–200	Not suitable for common crops. Usually devoted to pasture.
Grade 4	600–1000	200–300	Almost worthless for farming or fruit growing.
Grade 5	1000–3000	Over 300	Worthless.
Grade 6	Over 3000	.....	Worthless.

114. Remarks on the Removal of Temporary Hardness of Water.

The temporary hardness of water is easily removed by adding lime to the water in an amount calculated from a determination of the temporary hardness, and allowing the precipitate to settle out. The lime and the calcium bicarbonate react as follows:

$$CaCO_3,\ H_2CO_3+Ca(OH)_2=2CaCO_3+2H_2O$$

114A. If a water has a temporary hardness of 40 parts per 100,000 parts of water, how many pounds of lime are required for 1000 gallons of water? (One gallon of water weighs 8.32 pounds.)

In treating water in this way, an excess of lime must be avoided, hence after stirring the lime thoroughly into the water, another clarified sample is titrated again, and the proportion of water to lime adjusted in the light of this last result. An excess of lime is objectionable if the permanent hardness is to be removed later by means of soda, etc., because the excess of lime would entail a loss of soda. When water with a high temporary hardness is to be used for ice making, this hardness must be removed, because the calcium carbonate makes the ice cloudy: in this case an excess of lime also is to be avoided. This softening of water is usually done by attendants of average intelligence: they are furnished tables which show the amount of lime to be added for different titration results. It is necessary to test the water constantly, because, in general, the composition of the water from any one source changes constantly, and often extensively. The following data taken from analyses of the water of the Colorado river at Austin, Texas, may serve to show how extensive such variation in the composition of a water may be. The results are in parts per 1,000,000.

Date of Taking Sample	Suspended Matter	Total Dissolved Solids
August 1, 1905	2,480	300
September 22	124	498
October 20	742	248
January 19, 1906	0	324
May 19	600	550
May 29	1,256	294

115. The Removal of Permanent Hardness in Waters.

Permanent hardness is removed by adding soda-ash (sodium carbonate) or tri-sodium phosphate to the water from which the temporary hardness has been removed. The dissolved calcium and magnesium salts react metathetically with these reagents because their carbonates or phosphates are insoluble. The amount of the reagent to be added is calculated from the analytical determina-

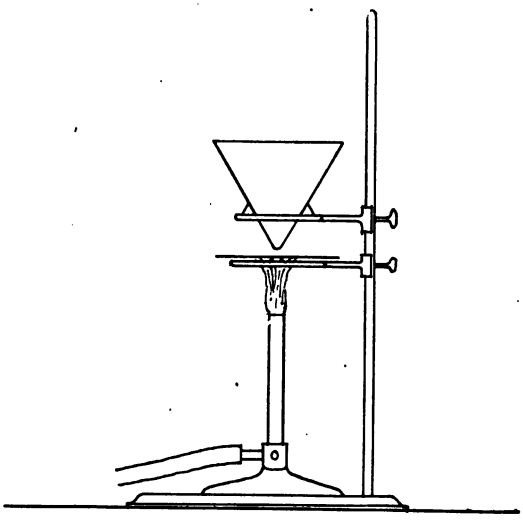
tion, given above, as follows: the number of parts of permanent hardness per 100,000 parts of water are multiplied by 1.22 to obtain the weight of sodium carbonate necessary for 100,000 parts of water, because $CaCO_3 : Na_2CO_3 : : 100 : 122$.

116. Calculate the cost of the sodium carbonate required to soften 1000 gallons of water which have a permanent hardness of 10 parts per 100,000 parts of water:—the cost of soda being 3 cents per pound.

117. The Determination of the Amount of a Saline Ingredient (Chloride or Sulphate) in a Water.

Optional quantitative exercise. Time required: 2 hours.

Secure an alundum filter and its support, suspend the filter in a clay covered triangle on a ring stand with a piece of asbestos board from 1 to 3 inches below it. Put a flame under the asbestos board at such a height that the filter will not be heated too strongly but will be dried out gently by the hot air. After ten to fifteen

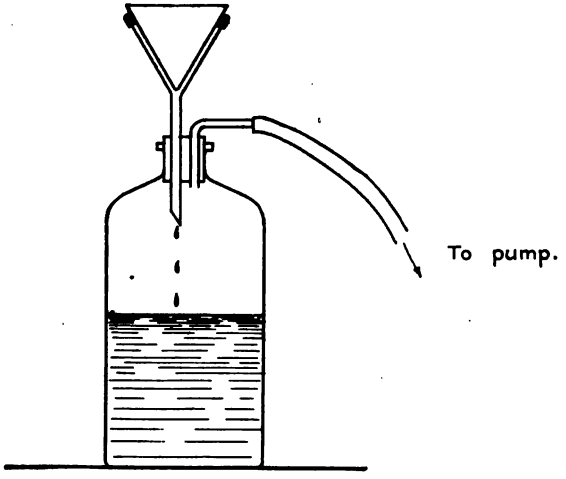


Method of drying precipitates.

minutes remove the burner, allow the filter to cool, and then weigh it accurately with its special support.

In the meanwhile measure out accurately 100 c.c. or 250 c.c. of a sample of water of which the chloride or sulphate content is to be determined. The amount of sample required depends upon the strength of the solution: the total amount of precipitate should be approximately 1 gram.

To determine the chloride content of a solution, acidify it with a few drops of dilute nitric acid, add 30 to 35 c.c. of a 3 per cent silver nitrate solution, stir the mixture with a glass rod but always leave the glass rod in the mixture and avoid splashing. When the upper portions of the liquid have cleared, add another drop of silver nitrate: if this shows that more silver nitrate is required, then add 5 c.c. of the solution and stir again. Test again as just shown. When all the chloride has been precipitated, then place the alundum filter on the suction funnel, turn on the water to operate the suction pump, pour the liquid into the filter in such a way as to transfer as much as possible of the precipitate to the filter (without spilling any of it!). Rinse the rest of the precipitate out of the beaker with distilled water slightly acidified with nitric acid and pour it into the filter. Fill the filter three



Filtration by suction.

times with acidified water, each time emptying it completely by suction. The filter and precipitate may then be considered to be free from salt solutions.

Next, dry the filter as before; then allow it to cool and weigh it again accurately. The difference between the first and the second weight is the weight of the silver chloride; from this calculate the weight of the chlorine in the precipitate—which is also the weight of chloride ion in 100 c.c. of the water.

If sulphates are to be determined, put the sample taken for this purpose into a beaker, add a few drops of dilute hydrochloric acid and heat the mixture to the boiling point. Add about 15 c.c. of

a 5 per cent solution of barium chloride and while stirring the mixture slowly keep it heated to the boiling point for several minutes (do not take the stirring rod out of the beaker!). Then add another drop of barium chloride solution to ascertain if enough of this has been used: if not enough has been used add a few c.c. more of this reagent. Stir and heat the mixture again. Test again as just directed. When precipitation is complete, place the alundum filter on the suction funnel, turn on the suction pump and pour the liquid into the filter in such a way that as much of the precipitate as possible is transferred to the filter without spilling any of it. Rinse the rest of the precipitate out of the beaker into the filter with distilled water slightly acidified with hydrochloric acid. Then fill the filter three times with acidified water and empty it each time completely by suction. The filter and the precipitate may now be considered to be free of salt solution.

Next, dry the filter as before, then allow it to cool, and weigh it. The difference between the first and the second weight is the weight of the barium sulphate: from this calculate the weight of the sulphate radical (SO_4) in the precipitate. This gives the weight of the sulphate ion in 100 c.c. of water.

CHAPTER X.

SOME EXPERIMENTS ON SILICA AND PHOSPHATES—TO ILLUSTRATE THEIR INDUSTRIALLY IMPORTANT PROPERTIES.

118. The Fusion of Silicates and the Preparation of Gelatinous Silicic Acid.

Put some sodium-potassium carbonate (fusion mixture) into a medium size porcelain crucible, put the latter on a clay covered triangle, and this in turn on the ring of the ring stand—in position to heat the crucible strongly with a burner. Secure some clean sand, grind a small amount of it as fine as possible in a mortar and put aside on a piece of paper as much of this ground sand as would amount to one-sixth of the bulk of the sodium potassium carbonate. Heat the fusion mixture, and when it is fused to a clear liquid sprinkle a little of this sand upon it: note the evolution of a gas (carbon dioxide) which results from the following reaction:—

$$Na_2CO_3+SiO_2=Na_2SiO_3+CO_2$$

When the first portion of sand has been acted upon, add another pinch and continue this. When the mass solidifies, move the stand with the crucible on it to a blast lamp, and remelt it with the aid of this blast lamp until all or most of the sand has been added and acted upon. Allow the crucible to cool, then put it into a small beaker, fill this half full with distilled water, and put away in a desk until the next laboratory period.

During the next period, pour the clear liquid into a dish, evaporate it to a small bulk, and allow it to cool; then add, drop by drop, dilute hydrochloric acid until the gas evolution ceases. A jelly-like mass (which is free silicic acid—H_2SiO_3) should separate from the solution during the addition of the acid. If it does not separate, evaporate the resulting solution until the silicic acid shows itself.

The fusion of silicates occurs in the fluxing of ores, in glazing pottery, in vitrifying bricks, and above all in the manufacture of glass. In all of this work the general fact is made use of that mixtures of silicates of two or more metals have lower fusing points than their components have separately,—and the fusion point of a mixture varies with the proportions of ingredients: the chemical engineer uses the table of the fusion points of the mixtures with different proportions and with their aid mixes the materials put into a furnace so that the mass may fuse at the lowest temperature.

119. Calcium Phosphate, Superphosphate of Lime, and Phosphoric Acid.

Weigh out roughly 31 grams of dry calcium phosphate or of bone-ash, put it into a dish and add 16 c.c. of concentrated sulphuric acid and 10 c.c. of water and stir the mass thoroughly until it has become a jelly. Then add about 100 c.c. of distilled water, pour the mixture into as tall a beaker as possible and allow it to remain there until the solid portion has settled to the bottom. Decant the clear liquid and evaporate it until it has a jelly-like consistency; this is mainly phosphoric acid.

The sulphuric acid and calcium sulphate are used above in the proportion required according to the following equation:

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4$$

If only two-thirds as much sulphuric acid is used, the substances will react according to this equation:

$$Ca_3(PO_4)_2+2H_2SO_4=2CaSO_4+H_4Ca(PO_4)_2$$

That is, when the calcium phosphate and the sulphuric acid are mixed in this proportion, the resulting mixture contains *primary* calcium phosphate together with calcium sulphate. This mixture is known as super-phosphate of lime and is used extensively to supply soluble phosphates in fertilizing a soil.

CHAPTER XI.

THE EFFECTS OF FORCES ACTING IN THE SURFACES OF CONTACT BETWEEN DIFFERENT SUBSTANCES.

120. It is a matter of common observation that oiled surfaces are not wetted by water, that water ascends in capillary tubes while mercury is depressed in such tubes, and that there are many other familiar phenomena which indicate that attractive forces exist in the surfaces between some substances while they appear to be absent in the surfaces between other substances. These surface forces are rather feeble, and hence they produce no noticeable effect as long as the extent of surface is small when compared with the amount of each substance enclosed by the surface; but when a substance is divided very finely, then the same amount of substance has a much greater extent of surface and then the quantity of effect produced by the surface forces becomes apparent. To show how the extent of surface of a certain amount of substance increases with its division into smaller particles, let us consider a solid with 1 cm. to the edge: it has a surface of 6×1 sq. cm. or 6×100 sq. mm.$=600$ sq. mm. This amount of substance divided into 1000 cubes of 1 mm. edge has a surface of $1000\times6\times1=6000$ sq. mm., and if each one of these particles is divided in the same manner into 1000 cubes, the surface of the total amount of the original cube is $1000\times1000\times6\times.01=60{,}000$ sq. mm. The latter is 100 times the surface of the original cube: whatever effect is produced by the surface forces when this substance is in contact with any other—say with water—then in the last state of division the amount of effect would be 100 times as great as when the material is in the form of a single tube.

121. Recent investigation has revealed that many substances suspended in water have particles ranging in size from one millionth mm. down to much less, even down to one millionth of a millionth mm. It is easily seen that substances in such fine states of division may exhibit remarkable surface effects. If the amount of substance in the cube above considered were divided into particles of the last size mentioned above (one millionth of a millionth mm.), then the surface effect upon that amount of substance would be 10,000 times as great when it is in the last form than when present as a single cube.

122. The most important action of surface effects that we have to deal with is the dissolution of solids in liquids. Recent investigations have shown more clearly than ever that the act of dissolution is merely a pulling or forcing apart of portions of the solid by the particles of liquid whereby the solid is broken up

into smaller particles. The forces that produce that action are the surface forces here referred to. According to the extent of subdivision — brought about by these forces, there are produced all kinds of solutions ranging in size of "dissolved particles" from particles large enough to be seen (as with starch or clay suspensions) to other solutions in which the particles are so small that the limits of physical division have been reached. The last are the solutions with which we have dealt so far: they are invariably solutions of crystalline substances.

The fact that dissolution depends on the action of surface forces is strikingly shown by the dissolution of tar oil in soap solution, an experiment that is given in the study of tar oil. In this experiment it is shown that water, or dilute soap solutions, do not "subdivide" tar oil globules in such a manner as to produce a "solution." Mixtures of tar oil and water are plainly seen to be heterogeneous in their composition: on remaining at rest they separate into distinct layers of oil and the aqueous portion and they can even be separated by filtration. Concentrated soap solution, however, produce with tar oil, homogeneous mixtures which cannot be separated into their components by physical means—they pass through filters just as ordinary solutions do. This difference in the ability of concentrated and dilute soap solutions to dissolve tar oil is coupled with the fact that the concentrated soap solutions have much greater surface tensions than the dilute; and hence it is not surprising that the surface forces between concentrated soap solutions and tar oils are able to produce dissolution while those between dilute soap solutions and tar oils are not.

123. Difference Between the Dissolution of a Crystalline Solid and of a Colloidal Solid.

In the dissolution of crystalline substances it is invariably observed that the solid bodies (crystals) are not affected internally by the liquid:—they do not "swell up," they do not become softer. The detached particles pass into solution all at once—through no noticeable intermediate stages: they are immediately subdivided to the limit of physical division.

However, in the dissolution of glue, of oatmeal, or of gelatine, etc., the progress of the action is in marked contrast to the progress of the dissolution of a crystalline body: the solvent penetrates the solid, and the particles at the surface are subdivided *gradually* until they are (practically) at the limit of subdivision, or until with a certain state of division the surface forces cease to be such as to produce further subdivision.

124. In the reverse change—the separation of solids from liquids—we have the same phenomena in reverse order. In the

separation of crystalline substances (e. g., in the separation of ice from water) a hard body is formed at once—without any intermediate stages—from the limpid liquid. There is no transition: it is a sudden change. The same is true when a salt crystallizes from its solution as the latter is concentrated. The particles separate from a limpid solution to form at once the final hard crystal and no amount of evaporation makes the liquid more concentrated or more viscous. However, when a solution of glue or gelatin is concentrated by evaporation, there is no sudden change: the liquid, together with the solid, passes gradually through all degrees of solidification,—the mixture becomes continuously more viscous and hence may attain, on drying, even enormous values of viscosity or "gluing power," so that a well glued piece of wood may break *beside* the joint rather than *in* the joint.

Since the behavior of glue or jelly is typical of the behavior of all non-crystalline substances, the latter are called *colloids,* which means resembling glue or jelly. Crystalline substances are called, similarly, *crystalloids.*

125. It can be shown that the plasticity or "stickiness" of clay is due to the presence of a colloidal solution between the solid sandy particles. For this purpose secure some good brick or potter's clay, shake up a small amount of it with distilled water and allow the mixture to remain at rest for twenty-four hours. It will be found that some of the finest particles of clay will remain in suspension indefinitely, and cannot be removed by filtration through ordinary filter paper:—they form a colloidal solution.

In contradistinction to the relation of the surface forces between clay and pure water, the relation between clay and salt water or lime water is such that clay is not "dissolved" by these solutions. Hence when lime water is added to a clay solution the dissolved particles separate from the solution and settle readily to the bottom. To show this, add a little lime water to the clay solution above prepared.

Next, work up a handful of clay thoroughly with water until the mass is quite plastic. Divide it into two portions; to one portion add a little slaked lime and mix the latter thoroughly with the clay. Notice the difference in the plasticities of the two portions. This difference shows itself well if the clay portions are shaped into rods and are then broken. Finally shape the two clay rods up again and put them away in your desk to dry. When dry, the one with lime will be found to be more fragile than the other. The reason for the difference is evident: the colloidal solution which glues the solid particles of the clay together is destroyed when the lime is added, and hence the clay looses its plasticity. If the colloidal solution within the clay is intact while the clay is drying, the latter becomes tougher and harder because the col-

loidal solution—which serves here as a glue—becomes tougher and more viscous *without limit* as it dries. The clay which dried without this binder is naturally more fragile.

126. The great strength of hydraulic cement is due to the same cause. However, with this substance the colloidal solution formed by a portion of the cement particles is not concentrated by evaporation, but through the removal of water by the formation of new hydrated compounds, which hydrated compounds form during the setting of cement.

The gluing power of freshly slaked lime is due to the fact that the slaking of the lime divides it into very fine particles which form a strong colloidal solution. *Air-slaked* lime is worthless for making mortar because on contact with water there is no slaking to break it into very fine particles. Wet mortar becomes worthless on long standing because the colloidal lime is precipitated gradually. If the mortar has dried in a wall as soon as possible the colloidal solution drys up before the colloid can be precipitated and hence the binding power of mortar remains intact after it has dried.

127. Besides the surface effect which distributes the solid throughout the liquid (dissolution), there is another noteworthy surface effect, which draws substances out of solution to the surfaces of solids. This is called *adsorption.* It is of frequent occurrence, but is not ordinarily noticed except with solids which are very finely divided, i. e., those which have a relatively great extent of surface. This phenomenon is strikingly illustrated in the following experiment:

Dissolve a dye—e. g., an Easter egg dye—in water, add to it some finely divided soil, stir the mixture for several minutes, and then filter it. A clear filtrate will be obtained, the color having been absorbed by the soil.

The adsorptive power of soils naturally produces many striking results, chief of which is the fact that many soluble substances *cannot* be leached out of soils by water; and again, that many dissolved substances such as potash salts, ammonium salts, etc., are taken out of solutions when they percolate through soils. In this adsorption of potash and ammonium salts, which are important plant foods, the adsorptive action appears as particularly beneficial. Of course there are other substances which, on account of a different relation between the surface forces, are not adsorbed; thus, sodium chloride is not adsorbed by soils from solutions, and soils are easily freed from sodium chloride by leaching.

128. Since adsorption is an effect produced by forces acting in the surface of contact between a liquid and a solid, it is to be

expected that the chemical nature of both will affect the result. A familiar illustration of this fact is seen in the action of dyes on different fibers: as a rule, direct dyes for cotton will not be adsorbed by wool (that is, they will not dye wool), and vice versa. At least there is a great difference in the intensity of the adsorption of the same dye by different fibers. This fact is so general that commercial dyes—e. g., diamond dyes, which see at any store—are put in *two sets,* one for wool and another for cotton. If desired, a trial may be made here with such dyes on well laundered white cotton and white woolen cloth or yarn.

129. In conclusion, some common useful applications of the properties of colloidal substances should be mentioned. Colloids, which, like gelatin, dissolve in any aqueous solution, evidently have such a relation of surface forces that their particles are strongly torn apart and kept apart:—if they are present in solution, together with other finely divided substances which are not drawn apart by their surface forces and which, if present alone, collect in larger particles and precipitates,—the latter are prevented by the former from collecting into larger lumps and precipitating. That is the case in inks in which the black pigment particles are kept apart by a gelatin solution. This is also the case in the silver chloride gelatin mixture used on photographic plates. The latter is easily shown by dissolving gelatin in water, adding some silver nitrate solution, stirring the mixture, and then adding sodium chloride solution: the precipitated silver chloride will remain finely divided and in suspension.

In other instances just the reverse action of colloids is made use of: if a clay solution has a little ferric chloride solution mixed with it and then some ammonia, it will be found that as the ferric hydroxide settles to the bottom the supernatant liquid is perfectly clear. This is due to the fact that the ferric hydroxide which could not remain in colloidal solution in such a medium draws the colloidal clay particles out of solution as it draws itself together to form larger particles.

CHAPTER XII.

ELECTROLYSES: THE CHEMICAL CHANGES AT THE POLES OF ELECTROLYTIC CELLS.

130. *Electrolysis* is the chemical decomposition of substances by means of a *direct* electric current. The latter must naturally be forced through the electrolytic cells by some outer agency such as a battery or a dynamo.

131. The poles of an electrolytic cell are given the same sign as the poles of the battery or dynamo to which they are connected. The *negative pole* is also called the *cathode,* because the cations move towards it while the current passes and the *positive* pole is also called the *anode* for the corresponding reason.

132. An Experimental Illustration of the Important Phenomena Involved in Electrolysis.

Secure eight small, porous earthenware cups—3 to 4 inches in height and 1½ to 2 inches in width; dip their upper edges into melted paraffin to a depth of 1 inch in order to close up the pores in these parts of the cups. Secure six rubber stoppers, two pieces of retort carbon about one-fourth inch in diameter and five inches in length, four pieces of thick *lead* wire (6 inches in length—Nos. 5 or 6 B. & S. wire gauge) several strips of sheet brass or "tin-can" plate, about one inch in width and five inches in length, and a similar piece of thin sheet copper or pieces of thick copper wire (12 inches in length, No. 12 or 14 B. & S. wire gauge) partly "coiled up" so as to fit into one of the "porous cups." The surfaces of these metal poles should be rubbed "bright" with sand paper.

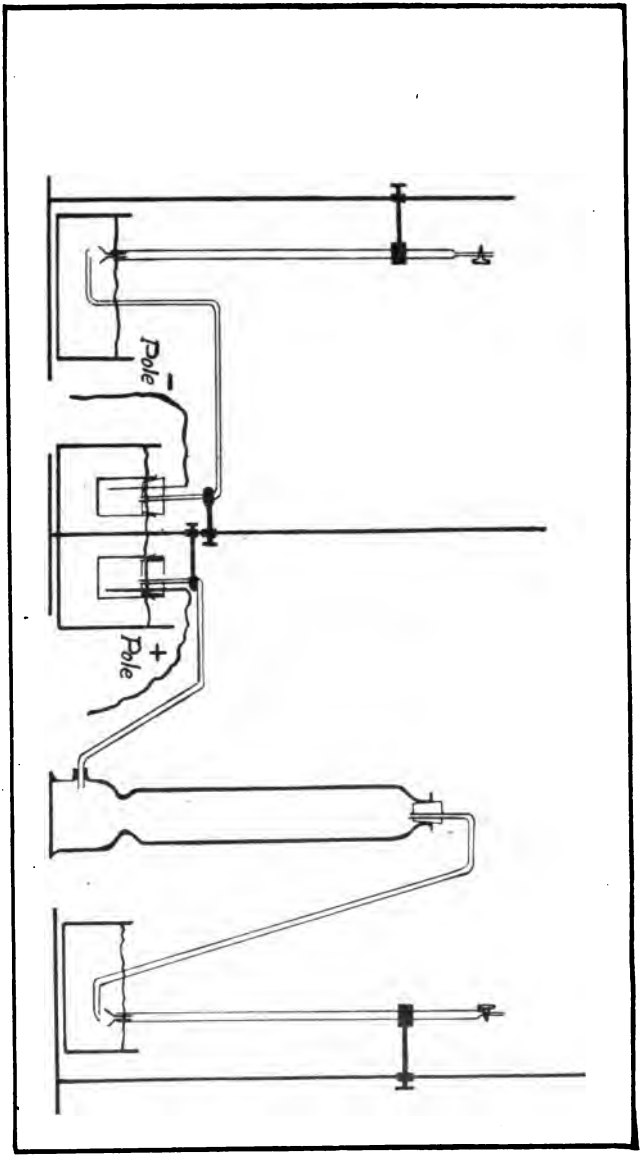
The cups are to be equipped as follows:

Cup 1—Closed with a rubber stopper through which extends a carbon pole and a delivery tube made from a glass tube twelve inches long and bent at the middle to a right angle. Fill with a mixture of equal parts of concentrated hydrochloric acid and water to which a few crystals of potassium permanganate or of potassium chlorate have been added in order to *saturate* the mixture with chlorine.

Cup 2—Open cup with a sheet of brass or "tin can plate" pole placed in it, and filled with a strong solution of copper sulphate.

Cup 3—Open cup with a copper pole, and filled with a strong solution of zinc chloride or sulphate.

Cup 4—Closed with a rubber stopper through which extends a



A Complete Electrolytic Cell.

carbon pole and the one-piece delivery tube shown on the left-hand side of the figure above. Fill with dilute hydrochloric acid.

Cups 5 and 6—Closed with rubber stoppers through which extend lead wire poles and delivery tubes as shown on the left-hand side of the figure above. Fill with dilute sulphuric acid.

Cups 7 and 8—Open cups with lead wire poles, and filled with sodium sulphate solution.

(a) Secure a beaker of such size that two of the cups may be placed in it; put cups 1 and 2 into the beaker and fill the rest of the space in the beaker with a saturated solution of common salt almost to the upper edges of the cups. Put an extension on the delivery tube of cup 1 so that the tube extends to the bottom of a tall, open-mouth bottle: the latter serves to collect and show the product—chlorine—which will be formed at this pole.

Twist the brightly polished ends of electrical connecting wires tight around the ends of the two poles: to secure firm connections, clamp the wire with a burette pinch clamp or a screw clamp. Connect the wires from cup 1 to the positive pole, and the wire from cup 2 to the negative pole of a suitable source of direct current (5 to 8 dry cells, or some source exerting 8 to 12 volts pressure).

After allowing the current to pass for two or three minutes, examine the appearance of the surface of the pole in cup 2, and the appearance of the gas discharged from cup 1 into the bottle. Copper has been deposited upon the pole in cup 2 by the discharge of copper ions; and chlorine—a greenish yellow gas of pungent odor—has been formed in cup 1 by the discharge of chlorine ions.

(b) Exchange cup 2 for cup 3, and repeat the operation:—zinc will be deposited on the pole in cup 3 by the discharge of zinc ions, while chlorine will continue to be formed in cup 1 as before.

(c) Exchange cup 3 for cup 4.

Secure a tall, slender bottle of at least one quart capacity, fit it with a rubber stopper and two glass tubes, one of which extends to the bottom of the bottle, while the other terminates just below the stopper. In place of this bottle the cylinder shown on the right-hand side of the figure above may be used. This bottle or cylinder serves to retain the chlorine, and allows an equal volume of air to be discharged in place of the chlorine. Air may be collected over water without appreciable loss, while chlorine cannot be collected over water because it is too soluble. Other glass tubes for connections should be bent as shown in the figure above. The ends of the delivery tubes which are to be placed under the burettes should be drawn out to a small opening. Secure two burettes and two dishes or beakers full of water. Place the burettes in position with the lower ends extending into the water,

and fill them by drawing up water by means of a piece of rubber tubing. By this means they may be quickly refilled when the experiment is to be repeated. Now join up the apparatus, and turn on the current, but allow the gases discharged by the delivery tubes to escape into the air instead of into the burettes. After electrolysis has been in progress for a minute or two, interrupt the current, place the burettes over the openings of the delivery tubes and turn the current on again. It will be found that the two gases are evolved at equal rates by volume. Hydrogen is formed in cup 4 by the discharge of hydrogen ions, while chlorine is formed in cup 1 as before.

(d) Exchange cup 4 for cup 5, but otherwise use the same equipment as with cups 4 and 1:—note that the two gases are again evolved at equal rates by volume, although the hydrogen is discharged from sulphuric acid in this case.

Since the reaction in cup 1 remains the same although the reactions in the different cups connected with it are different, it follows that the action at this pole is independent of the action at the other pole. *This is always true.* It will be illustrated again by connecting cup 6 in place of cup 1, and placing cup 6 in the beaker together with cups 2, 3, 4, and 5 in turn. The reaction accompanying the passage of the current through cup 6 connected to the positive pole of the battery results in the production of oxygen.

(e) Cup 2 with cup 6:—use a fresh piece of brass for the pole in cup 2 in order that the deposit of copper may show itself. Collect the oxygen from cup 6 in a test tube over water, and test it with a glowing splinter.

(f) Cup 3 with cup 6:—Repeat as directed with cups 2 and 6.

(g) Cup 4 and cup 6:—Collect both the hydrogen and the oxygen in inverted burettes over water. The hydrogen is evolved twice as fast by volume as the oxygen.

(h) Cup 5 and cup 6:—Repeat as with cups 4 and 6.

(i) Put cups 7 and 8 into the beaker filled with salt water. Test the contents of the cups with litmus paper:—they should not affect litmus. Connect cup 7 to the negative pole of the battery and cup 8 to the positive pole, and after the current has passed for five minutes, test the contents of cup 7 with red litmus paper, and the contents of cup 8 with blue litmus paper. Both will be changed to the opposite tints. Note also that gases are evolved in both cups (possibly in small amounts only because the amount of current passing is small):—hydrogen is evolved in cup 7 and oxygen in cup 8.

Take the apparatus apart and place the porous cups in distilled water to leach out the solution contained in the pores. Salts

crystallizing in the pores would crack the jars, as the water evaporates.

Make definite entries of all results in your note-book.

Before taking up the theory of the changes in these "electrolytic" cells, it is necessary to learn something concerning the nature of electricity itself.

133. The Present Day View of the Nature of Electricity.

Experiments have revealed the existence of a distinct kind of matter made up of such small particles that about one thousand of them would weigh as much as a single hydrogen atom. These particles appear to be composed of definite quantities of negative electricity. They are called "electrons." They are given off by metals under certain conditions (by hot wires in vacuum tubes) almost as vapors are given off by liquids. During the passage of a (direct) electric current through a highly rarified vacuum tube, "rays" or "streams" of electrons are projected in straight lines from the cathode (negative pole), and their impacts upon the glass walls render the latter luminous. These and many other facts serve to show that negative electricity is a distinct substance capable of existing apart from all other matter. When it is "lodged or located upon," or "combined with" other *neutral* matter, the latter is said to be charged negatively.

"Rays" or "streams" of particles composed of nothing but positive electricity similar to those of negative electricity (electrons) *have never been observed:* the positive charge seems to be only a condition of matter—not a substance itself—and a positive charge on a substance means that the substance has *then* a lesser number of electrons than it has when it is in the electrically *neutral* condition.

Since electrons are obtained from metals, it is thought that the latter contain free electrons—and that an electric current passing through the wire is like the moving of a gas through a tube: during this operation any part of the wire receives from one side as many electrons as pass from it towards the other side, hence every part of the wire contains afterwards as many electrons as before. A certain number of electrons appear to be necessary for the metal atom to be electrically neutral:—if the number of electrons on a metal atom becomes less than this, it is charged positively—as for instance, the metal ions in solution. If a neutral atom has electrons added to it, it is charged negatively—as for instance, the atoms of non-metals (chlorine, bromine, sulphur) and the acid-radicals.

According to this view, when a salt ionizes (in solution), the metal in each molecule gives up one or more electrons (*one* for every valence) to the acid radical.

134. The Theory of the Changes in Electrolytic Cells.

In accordance with the *Electron Theory* outlined above, the changes at the cathodes or negative poles of electrolytic cells take place as follows:—the "pumping" action of the electric battery forces the electrons through the connecting wires to the cathode, and from this into the surrounding solution where they neutralize (combine with) the positive charges on the cations—copper, zinc, hydrogen:—in the neutral state, these substances exist in the ordinary form in which we know them as *metallic* copper, metallic zinc, and gaseous hydrogen. During the same period of time, an equal number of chlorine ions which are next to the surface of the anode give up their negative charges or electrons to the pole, thus changing to neutral chlorine, or ordinary gaseous chlorine. It should be noticed that during the same period of time just as many electrons pass from the connecting wire into the cell at the cathode as are sent *out* of the cell at the anode into the connecting wire.

With this discharge of cations at the cathode, the portions of the solution from which they are taken are left momentarily with more anions than correspond to the cations present. At the anode, the discharge of anions leaves these portions of the solution momentarily with more cations than corresponds to the anions present. On account of their electric charges, these unbalanced anions at the cathode tend to draw together with cations in adjacent drops of liquid so that they may be in drops of liquid which contain an equal number of positive and negative charges: the anions thus displaced in these adjacent drops tend to do the same with the cations in the drops still farther on, etc. At the same time the cations which remain unbalanced at the anode tend to draw together with the anions in drops adjacent to them: these two tendencies, communicated from drop to drop, extend from cathode to anode and they bring about a slight shift of all the cations towards the cathode and of all the anions toward the anode in order that those ions which were temporarily left unbalanced at the poles may be placed in drops in which they are perfectly balanced with an equal number of opposite kinds of ions,—and, also, that all other ions in intermediate drops are similarly balanced. Note that each shift moves the ends "of these lines farther from the poles": thus the solutions next to the poles become more dilute. Furthermore, some kinds of ions move more easily than other kinds, hence this mutual attraction may move one set of ions a small fraction, say, one-fourth *of the total distance through which both are to be moved*, while it moves the other set of ions much farther, say, three-fourths of the total distance.

This motion of the ions which accompanies the actions at the poles is designated "the electric transport of the ions."

Evidently, the passage of a current through an electrolytic cell produces three distinct and independent actions: the two pole actions and the transport of the ions. This fundamental fact is the key to the study of electrolysis.

The discharge of the ions *copper, zinc, hydrogen* and *chlorine* requires no further explanation; but the discharge of oxygen out of solutions of sulphate anions (cups 6 and 8) as well as the discharge of *hydrogen* out of solutions of sodium cations (cup 7) requires further consideration.

To understand these actions it must be known that a very much greater force (voltage) is necessary to discharge sodium ions than to discharge hydrogen ions from water,—hence with a moderate electromotive force only the H^* ions from water are discharged and the OH' ions remain to render the liquid alkaline: the excess of anions thus formed at the cathode is equalized by "transport."

In cups 6 and 8 (anodes), the O'' ions from water are evidently discharged—probably because the force required for this action is less than the force required for the discharge of the SO_4'' ion. The discharge of O'' ions leaves the H^* ions from water to render the liquid *acid* (cup 8), and the excess of cations thus produced is equalized by "transport."

The transport action does not necessarily move the same ions as those which are discharged at the poles. Thus in cups 7 and 8, in which the ions of water (hydrogen and oxygen) are discharged, it is not these, but the ions Na^* and SO_4'' which are moved by the electric transport.

135. The fact that hydrogen and chlorine are liberated in equal volumes by the same amount of electric current is a fact which should be noted; and in this connection it should be pointed out that although these gases were in no sense obtained by the direct decomposition of HCl, yet they are here obtained in the same proportion by volume in which they combine to form hydrochloric acid gas.

The same is true in regard to hydrogen and oxygen, which are here obtained in the ratio by volume of 1:2: this is the same ratio as that in which they combine to form water.

CHAPTER XIII.

BATTERY CELLS AND OXIDATION AND REDUCTION REACTIONS.

136. Under this heading we will take up the study of reactions which, in contradistinction to metathetical reactions, involve changes in valence. The following are some reactions of this kind which have been met before,—the valences of the *changing* substances are marked:

$$Zn^{\circ}+2H^{*}Cl=Zn^{**}Cl_2+2H^{\circ}$$
$$Zn^{\circ}+Cu^{**}SO_4=Zn^{**}SO_4+Cu^{\circ}$$
$$O^{\circ}\text{ (from an oxidizer)}+2HCl'=H_2O''+2Cl^{\circ}$$
$$KBr'+Cl^{\circ}=KCl'+Br^{\circ}$$
$$2H^{\circ}+O^{\circ}=H_2O''$$
$$H^{\circ}+Cl^{\circ}=H^{*}Cl'$$

In these, as in *all* O. & R. (oxidation and reduction) reactions, there are always *two* distinct substances which undergo valence-changes (in opposite senses!).

Valence changes have been met before, in the study of electrolytic cells: when copper is deposited from a copper salt solution the change may be expressed thus,—

$$Cu^{**}+2(-)=Cu^{\circ}$$

When chlorine is discharged during electrolysis from a chloride solution the change that occurs at the positive pole (anode) may be expressed thus,—

$$Cl'=Cl^{\circ}+1(-)$$

Evidently the symbol (-) is used to denote an electron.

All valence changes in O. & R. reactions are due to the giving up of electrons just as the changes which take place at the poles of the electrolytic cells are due to this.

137. The *cause* of O. & R. reactions is the natural tendency to change so as to give up or take up electrons which many substances possess. The tendencies of the oxidizer and that of the reducer may reinforce each other, or the greater tendency of one may overcome the opposing tendency of the other.

The electrons are always taken up by one valence-changer as the other one gives them up, and this adjusts the ratio in which the two are changed. Note how this is shown in the reactions given above.

138. Definition of Oxidation.

The term oxidation does not only include the changes in which oxygen appears as having combined with the substances said to be oxidized, but it also includes such changes as the conversion of any free metal to any of its salts (Cu to $CuCl_2$) and the liberation of a non-metal from its salts such as the liberation of chlorine from hydrochloric acid or from sodium chloride. The term oxidation has been extended so as to include these changes because when they are brought about in one way they certainly involve oxidation, and hence when they are brought about in any other way they are also considered as involving an equivalent change. Thus in the above example the Cu may be oxidized first to CuO and then by reaction with HCl it is changed to $CuCl_2$ and since the latter change does not undo the first oxidation, the Cu in $CuCl_2$ is still in the same state of oxidation as it was in CuO. Hence whenever Cu is changed to $CuCl_2$ the change involves something equal to oxidation and is spoken of as oxidation. Again, chlorine can be produced from hydrochloric acid by reaction with oxygen; hence whenever a chloride is acted upon so as to produce free chlorine by any means whatever the operation is considered to be equivalent to oxidation and is spoken of as such.

In order to define oxidation in a simple manner yet so as to include all changes now included under this term we say: Oxidation is any change that involves the giving up of free electrons. Point out which substances are oxidized in the reactions above—which reduced.

139. The Connection Between Oxidation-Reduction Reactions and Battery Poles.

If we use a mechanical arrangement such as was used for electrolytic cells, and place one valence-changer of an O. & R. reaction at one pole and the other valence-changer at the other pole, we will obtain an arrangement which will send out a current through the wire connecting the poles. Such an arrangement is called a battery cell. When the two valence-changers of an O. & R. reaction are thus placed apart at the poles of a battery cell, they undergo the same changes as they do when acting directly upon each other. Hence it is seen that the action of a battery pole shows, in the simplest form, the action of the valence-changer in it; and to learn the action of the different valence-changers, we need but study the behavior of the poles made up from them.

This study of valence-changers is simplified immensely by the fact that the two poles in a battery cell act independently of each other (just as the actions at the poles of electrolytic cells take place independently of each other); the action of a valence-changer or battery pole will hence be the same in different com-

binations, and can be learned, once for all, from any one combination. For this reason all valence changers will be studied first as battery poles.

140. Algebraic Signs of Poles.

(a) Electrolytic cells are those through which a current is forced by some outer agency: the operator is interested only in the current as sent into the cells, and he naturally calls that pole the negative pole at which the electrons flow *into* the cell.

(b) Battery cells are those which supply current: the operator is interested only in the current which flows out of the cell, and he naturally calls that pole the negative pole where the electrons come out of the cells.

141. The Components and the Action of Battery Poles.

In order that a battery pole may act properly when combined with any other pole it must be equipped so that it may act either as a positive or as a negative pole. This is made possible by placing, in immediate contact with the pole, the two chemical forms of the valence-changer which are so related that one is the product produced from the other when the pole acts in one sense, while the latter is changed back to the former when the pole acts in the opposite sense. The following arrangements illustrate this:

(a) Zinc metal dipping into a zinc salt solution: when this pole acts as the negative pole of a combination, then zinc metal changes to zinc ions; and when it acts as the positive pole, zinc ions are discharged and yield zinc metal again.

(b) Hydrogen gas in any acid (solution of hydrogen ions): when the pole acts as a negative pole, hydrogen gas changes to hydrogen ions; and when the pole acts as a positive pole, hydrogen ions change to hydrogen gas.

(c) Chlorine gas in a solution of a chloride (chloride ions): when this pole acts as a positive pole, chlorine gas changes to chlorine ions; and when it acts as a negative pole, chlorine ions change back to chlorine gas.

The action of these poles will now be considered in detail.

(1) A zinc rod dipping into a zinc salt solution: by direct dissolution of the zinc (or perhaps indirectly) the solution is saturated with metallic zinc—particularly the liquid adjacent to the metal rod. This dissolved zinc metal, just as all metals, reacts according to the following equation:—

$$Zn^{\circ} = Zn^{**} + 2(-)$$

But in the study of electrolysis we learned that electrons combine with metal ions to form the free metal,—which, in the case of zinc would take place according to the equation—

$$Zn^{**} + 2(-) = Zn^{\circ}$$

This reaction is the reverse of the one above, and hence there are two opposing tendencies acting in this pole. When the pole is at rest, i. e., not sending a current in either direction, there must be a certain concentration of electrons present within the pole with which the two opposing tendencies are equal. If this pole acts as a negative pole, i. e., if electrons are allowed to flow out of the pole, then the pole material will change so as to produce electrons, hence it reacts in this sense:

$$Zn^{\circ} = 2(-) + Zn^{**}$$

But if the pole acts as positive pole, i. e., if electrons are poured into the pole, the pole material will change so as to use up electrons, hence it reacts in this sense:

$$Zn^{**} + 2(-) = Zn^{\circ}$$

The voltage or potential of a pole is the force with which it tends to send out electrons over the connecting wire, or the force with which it opposes the sending into it, of electrons, over the wire: this force is naturally proportional to the concentration or state of compression of electrons in the pole. The voltage or potential of a pole is measured while the pole is *at rest* because then the electron concentration in the pole is that with which the materials are in equilibrium.

(2) Hydrogen gas in an acid solution: this pole must be provided with an extra conducting rod to conduct the electrons into or out of the solution. For this purpose a material must be used which, itself, undergoes no change in this mixture, and the most suitable materials for this purpose are platinum, gold, and graphite. The solution is saturated with hydrogen gas by allowing the gas to bubble through the solution constantly.

The action of this pole is due, on one hand, to the tendency of hydrogen gas to change to hydrogen ions, according to the equation:

$$H^{\circ} = 1(-) + H^{*}$$

But when electrons are added to hydrogen ions, they change back to hydrogen gas, according to this equation:

$$H^{*} + 1(-) = H^{\circ}$$

Hence, as with zinc, so with hydrogen, the pole reaction is reversible, and there are two opposing tendencies acting in this pole. When at rest, the pole contains a certain concentration of electrons with which the two opposing tendencies in this pole are in equilibrium. Naturally, the concentration of electrons in this pole is different from that in the zinc pole.

If this hydrogen pole acts as a negative pole—to allow electrons

to flow out of the pole—then the pole material must react to produce new ions, which it does according to the reaction:

$$H^\circ = 1(-) + H^*$$

But if the pole acts as a positive pole, i. e., if electrons are poured into the pole, the pole material will change so as to use up electrons, according to the equation:

$$H^* + 1(-) = H^\circ$$

(3) Chlorine gas in a solution of a chloride: again a non-reactive conductor of platinum, gold or graphite is necessary. The pole reaction here is:

$$Cl' = 1(-) + Cl^\circ$$

The details of the actions in this pole correspond in every respect to those in the hydrogen pole. The free electron concentration which exists in the pole at equilibrium is naturally again different from those in the poles above.

When this pole acts as a negative pole, the actual change which takes place in this pole is:

$$Cl' = 1(-) + Cl^\circ$$

because this change tends to replace the electrons which have flown out over the wire while the pole is acting as a negative pole. When this pole is acting as a positive pole, it reacts thus:

$$Cl^\circ + 1(-) = Cl'$$

because this reaction takes up the new electrons which are poured into this pole while it acts as a positive pole.

The electron concentrations are really not known, but we know that the voltage or electromotive force between two poles combined to form a battery cell is directly related to their electron concentrations; and hence, to measure in a sense, the electron concentrations in all poles, we select one pole, combine all other poles, in turn, with it, and measure the voltage of each combination. In the table of battery poles given at the end of this chapter, the common pole used is a hydrogen pole, like that described above; and the poles have been so arranged in the table that *they appear in the descending order of their electron concentrations.* It should be noticed that for each pole the concentrations of both the reduced and the oxidized states of the valence-changer are definitely given: without this definition of these concentrations, the electron concentrations would be *indefinite* and hence the potentials would have no definite value.

142. Details of Action When Two Poles are Combined to Form a Battery Cell.

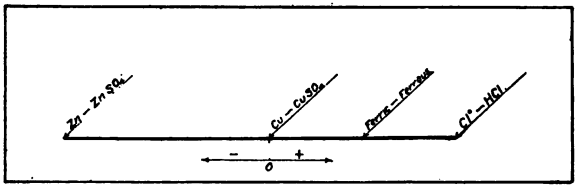
When two poles are combined into a cell as is shown below, the electrons will naturally flow through the connecting wire from the pole in which they are most concentrated to the pole in which they are less concentrated. The pressure acting to send the current is the difference between the electron pressures of the two poles: this pressure is proportional to the voltage of the cell.

The two poles of a battery cell must be connected by a salt solution for the same reason for which the poles of an electrolytic cell must be thus connected:—while the cell is sending a current through the wire from one pole to another, the reaction taking place at one pole will result in the temporary presence of an *excess* of *cations* over anions in that region, and the action at the other pole will result in an excess of anions over the cations in the latter region, and these two excesses are equalized by the double shift of ions throughout the solutions extending from pole to pole, as was pointed out in the study of electrolytic cells.

143. Demonstration of the Action of Battery Poles.

Secure five porous cups like those used in the experiment on electrolytic cells, a beaker large enough to hold two porous cups standing side by side, a sensitive voltmeter with a range of two volts or only slightly more, and two electrical connecting wires. Equip the five cups as follows:

Cup 1—Put in a strip of bright sheet copper about one-half inch in width and five inches in length, or a small coil of stout



Plot of Pole Voltage.

copper wire (about No. 14); fill with strong copper sulphate solution.

Cup 2—Put in a rod of zinc about five inches long, and fill with strong zinc chloride or zinc sulphate solution.

Cup 3—Put in a rod of cadmium and fill with a cadmium salt solution.

Cup 4—Put in a thin rod of carbon; fill with a mixture of equal parts of concentrated hydrochloric acid and water:—and saturate the liquid with chlorine by adding a few crystals of

potassium chlorate or permanganate which liberates chlorine by oxidizing some of the hydrochloric acid.

Cup 5—Put in a thin rod of carbon, fill with a solution of a bromide to which some bromine has been added. A solution of iodine in potassium iodide may be used in place of the bromine and bromide.

Put cup 1 (the copper pole), together with cup 2 (the zinc pole), into the beaker with salt water, and connect the poles to the voltmeter in such a manner as to make the needle deflect properly; for this purpose it is necessary to connect the zinc pole to the negative connector of the voltmeter. We say, the zinc pole is "negative" to the copper pole. The reading should be about 1.10 volts. Next, make a "line plot" of this measurement: draw a line about 6 inches in length, lay off on it about 20 equal parts, each to represent 0.1 volt. Put a minus sign at the left end of the line, and a plus sign at the right end. Select any division point, one or two divisions to the right of the mid-point, and mark it "Cu-pole." To indicate that the zinc pole is *negative* to the copper pole, *place it toward the left* of the "Cu-pole," at a distance corresponding to the reading. An illustration of the plotting of pole voltages is shown in the accompanying figure.

Couple the cadmium pole with the copper pole, and "plot" the reading on the same line. The reading should be: cadmium pole negative to the copper pole, about 0.7 volts.

When a "copper" pole is combined with a "zinc" pole, the voltmeter connection shows that the latter is negative, which means that electrons formed at the zinc pole come out through the wire. Hence, of the two opposite directions in which the material in the zinc pole could react—

$$Zn^{\circ} \rightleftarrows Zn^{**} + 2(-)$$

the one indicated by the upper arrow takes place. At the copper pole, electrons flow in from the wire and are used up—hence of the two possible reactions—

$$Cu^{\circ} \rightleftarrows Cu^{**} + 2(-)$$

the one corresponding to the lower arrow takes place.

When a cadmium pole is coupled with a copper pole, the cadmium acts just as the zinc does in the preceding case.

Since the measurements show that the concentration of the free electrons in the zinc pole is so much greater than in the copper as to cause a pressure of (about) 1.1 volts, while the difference between the electron concentrations of the cadmium pole and the copper is only such as to cause a pressure of .74 volts, it follows that the concentration of the electrons in the zinc is greater than

in the cadmium by such an amount as to cause a pressure of 1.10—.74=.36 volts. This is also shown by the line plot:—here the number of spaces between the zinc and cadmium poles is 3.6 spaces (=.36 volts) and the zinc "is negative to the cadmium" because it is further toward the negative end.

144. Ascertain experimentally the voltage of a "cell" by coupling the zinc pole (cup 2) with the cadmium pole (cup 3).

The agreement between the values read from the plot and the values observed in this experiment shows that in the different combinations each pole is exerting the same "tendency to change," i. e., its action is independent of the other pole with which it is connected.

In this combination the cadmium pole acts as the positive pole, hence it changes in the reverse sense from that in which it changed before. The change now is—

$$Cd^{**}+2(-)\rightarrow Cd^{\circ}$$

But the zinc pole acts as before.

145. Measure the voltage of the cell formed by coupling the chlorine pole with the copper pole (cup 4 with cup 1) and plot the result. Measure the voltage of the cell formed by coupling the bromine pole (or the iodine pole) with the copper pole, and plot the result.

Finally, measure the voltage of the cell formed by coupling the chlorine pole with the bromine pole and compare the result with the relation between these poles shown by the plot above.

When the copper pole is connected with the chlorine pole the copper pole is the negative pole in this combination: to *produce* electrons, the copper metal must change according to the reactions:

$$Cu^{\circ}\rightarrow Cu^{**}+2(-)$$

Since the chlorine pole is the positive pole it follows that in it that particular change must be going on which uses up electrons,—which is the change from free element to ions according to the reaction°

$$Cl^{\circ}+1(-)\rightarrow Cl'$$

When a bromine pole (bromine in KBr solution) is connected with the copper pole, the bromine acts in exactly the same manner as the chlorine above.

But when the bromine pole is connected with a chlorine pole the bromine pole acts as the negative pole,—hence that particular reaction will take place in this pole which will produce electrons, i. e., bromine ions change to free bromine according to the reactions—

$$Br'\rightarrow Br^{\circ}+1(-)$$

The chlorine pole acts as before.

146. Measure the voltage between the zinc pole and the chlorine pole, and compare the result with the relation between these poles shown by the plot above. State the pole changes taking place in this cell while the current flows.

Do the same with the cadmium pole and the bromine pole.

THE TWO POLE ACTIONS OF A BATTERY CELL CONSTITUTE AN OXIDATION-REDUCTION REACTION; AND VICE VERSA.

147. Put a few pieces of granulated zinc into a test tube, barely cover them with copper sulphate solution, and shake the mixture until the blue color of the copper ion (?) has disappeared. Note the metallic copper formed. Pour some of the resulting liquid into another test tube, add a little ammonia, and test with H_2S. The formation of a white precipitate (ZnS) shows that zinc has been changed to a salt. The reaction in the mixture above is—

$$Zn^{\circ}+Cu^{**}SO_4=Zn^{**}SO_4+Cu^{\circ}$$

This reaction is evidently the sum of the two pole reactions—

$$Zn^{\circ}=Zn^{**}+2(-)$$
$$Cu^{**}+2(-)=Cu^{\circ}$$

which are the two pole actions that take place in the cell above formed by coupling the copper pole (cup 1) with the zinc pole (cup 2). This test tube with zinc and copper sulphate solution contains all those parts necessary for the action of the cell "cup 1 with cup 2," because in this cell only *zinc* and *copper ions* are changed. If we imagine the two poles and pole liquids brought together so that the poles touch, then no connecting wire is needed and the salt solution between the cups also is unnecessary. The test tube, hence, contains all necessary parts of the *whole cell.* The same force which is active in the battery cell above is the force which brings about the reaction in the test tube mixture.

In this action evidently zinc is oxidized and copper ion is reduced—the *amount of oxidation* being equal to the amount of reduction because zinc cannot change without getting rid of electrons and copper ion cannot change without receiving electrons. Hence the quantity of each substance which is changed depends upon the number of electrons transferred from the zinc to the copper ion.

148. If cadmium metal is put into some copper sulphate solution, what reaction will take place? Of what two pole actions is it the sum? Which substance is oxidized, which reduced? Answer the same questions for a mixture of zinc and cadmium sulphate solution.

149. Put some granulated zinc into a test tube, add a little bromine water (or iodine solution), and shake the mixture until the color has disappeared. Test the solution for zinc ion as in the preceding experiment.

The action in this mixture is identical with the action in the cell formed of the zinc pole (cup 2) together with the bromine pole (cup 5). Write the pole equations and add them up to obtain the action in this test tube mixture. State what is oxidized, what reduced.

150. Recall (or try now) the reaction between potassium bromide (or iodide) solution and chlorine water. To what battery cell above does this mixture correspond? What is oxidized? What is reduced?

151. Exercise on the Table of Battery Poles.

1. Note the relative positions of the metal poles and of the halogen poles in the table of battery poles (at the end of this chapter) and fix them in your memory. The relative tendencies to reaction indicated by the position of these substances in the table is not changed extensively by diluting or concentrating the solutions in the poles; only when very large differences in concentration occur such as between the hydrogen ion concentration in an acid on one hand and in pure water on the other (the latter contains one-ten millionth as much H ion as the former!), then the voltage of the same material may have largely different values, and hence, corresponding to different concentrations, the same material may appear at several different places in the table. These are the exceptions, however.

In general, the positions of these elements in the table indicate the relative ease or difficulty of extracting them from their common compounds (oxides, chlorides, sulphates, nitrates, carbonates, etc.), or conversely, it indicates their relative tendency to form these compounds.

Ascertain from your text what metals are frequently found in the earth in the form of free metals,—which rarely,—and which are never found as free metals:—relate your findings to the order of the metals in this table.

2. Will copper react with a solution of a mercury salt? (Make a test tube trial!). What metals liberate hydrogen from acids? How must two metals be related in position in the table in order that one placed in a solution of a *simple* salt of the other will reduce the latter?

3. How must the non-metals—oxygen, sulphur, chlorine, bromine, iodine—be related in position in the table in order that one mixed with a solution of a "salt" of the other will oxidize the latter?

4. Note the position, in the table of battery poles, of the pole which is composed of solutions of ferrous and ferric salts, the pole reaction of which is expressed by the equation:

$$Fe^{**}=1(-)+Fe^{***}$$

Select from the table a list of substances which when added to a solution of a ferric salt will reduce this to a ferrous salt; select also a list of substances which when added to a solution of a ferrous salt will oxidize this to a ferric salt.

Of the substances thus selected, the following *should be remembered* because they are frequently employed in experimental work:

(a) Common reducing agents,—the metals, from magnesium to tin, and hydrogen sulphide.

(b) Common oxidizing agents,—bromine, chlorine, nitric acid, bichromates and permanganates.

5. The oxidation of ferrous salts is now to be experimentally demonstrated. In this experiment we make use of potassium sulphocyanate—KCNS—for the purpose of showing the presence or absence of ferric salts: it reacts with ferric salts to produce a deep red solution—of ferric sulphocyanate—but it produces no color with ferrous salts.

Secure a small amount of ferrous salt solution which has been kept in contact with fine iron filings: this solution should give no color with potassium sulphocyanate (test a few drops of it). To a few c.c. of this ferrous salt solution, add a few drops of concentrated nitric acid and heat the mixture. Does it give any indication that a reaction has taken place? Add a few drops of the sulphocyanate to it; what does the result indicate? To another portion of the ferrous salt solution, add a few drops of a solution of iodine (in potassium iodide): note the disappearance of the iodine. Test the mixture for the presence of ferric salts. Treat a third portion of the ferrous salt solution with a few drops of a solution of potassium permanganate plus a few drops of sulphuric acid: the disappearance of the color indicates that the permanganate has been reduced. Test the mixture for ferric salts.

6. The reduction of ferric salts is now to be demonstrated. Secure some ferric chloride solution. To a small portion of this, add small amounts of stannous chloride solution until the mixture is free from ferric salt (as ascertained by treating a small amount of the mixture with sulphocyanate). Reduce another portion with hydrogen sulphide gas by passing this gas through the *warmed* solution, until a test shows it to be free from ferric salts.

7. Further illustration of oxidation=reduction reactions are obtained by the oxidation of hydrogen sulphide by (a) nitric acid, (b) bichromate solution acidified with dilute sulphuric acid, (c) permanganate solution acidified with dilute sulphuric acid: pass

hydrogen sulphide into warm dilute solutions of these substances. Note carefully all indications that the mixtures have reacted.

9. Write the equations for the reactions which occur above in the following mixtures:

ferrous salts and iodine;
ferric chloride and stannous chloride;
ferric chloride and hydrogen sulphide.

The reaction with nitric acid, permanganate, and other ternary compounds should not be attempted now. It is the object of the following sections to show how such complex substances are to be considered in oxidation-reduction reactions.

THE BACK ELECTROMOTIVE FORCE IN ELECTROLYTIC CELLS.

From the table of battery poles ascertain the voltage of a cell made up of a copper pole and a chlorine pole. In which direction would the electrons flow through the wire connecting the poles? Hence what chemical change would take place at the copper pole? At the chlorine pole? In order to *reverse* these changes, the flow of the current would have to be *reversed:* if a dynamo is connected into the wire connection between the poles so as to oppose the voltage of the cell, what voltage must the dynamo *exceed* in order that the current will be *forced* in the reverse direction? Then the cell would not be a battery cell, but an electrolytic cell:—what chemical changes would then take place in the cell?

152. The last question shows how an opposing electromotive force in an electrolytic cell may be produced: the products formed at the poles of all electrolytic cells exert an opposing electromotive force just as large as that which these materials exert as battery poles. Thus when hydrochloric acid is electrolyzed between platinum poles, the discharged hydrogen at the cathode, and the discharged chlorine at the anode, form battery poles with an electromotive force between them of about 1.35 volts (see table), and hence the applied electromotive force must exceed this amount to be able to force a current through the electrolytic cell.

153. In order that cadmium and bromine be discharged by electrolysis from a solution of cadmium bromide, what minimum value must be exceeded by the applied electromotive force? In order that hydrogen and oxygen may be discharged, by electrolysis, from dilute sulphuric acid, what minimum value must be exceeded by the applied electromotive force?

Of several different metal ions (cations) present at a cathode during electrolysis, the one which is lowest in the table of bat-

tery poles will be discharged first. Thus if a mixture of solutions of silver and copper salts is electrolyzed, only silver will be deposited at the cathode (provided the current is moderate).

Of several anions present at an anode during electrolysis, the one which is *highest* in the table of battery poles will be discharged first. Thus if a mixture of solutions of iodides and chlorides is electrolyzed, only iodine is discharged at the anode (by a moderate current!).

154. If a mixture of solutions of copper chloride and potassium iodide is electrolyzed between platinum poles, what will be discharged at the cathode, what at the anode?

All the fundamental principles of "oxidation-reduction" reactions have now been illustrated. The further study of these reactions consists of becoming acquainted with other common valence-changers, and learning the particular chemical changes they undergo when acting as oxidizing (or as reducing) agents. A number of valence-changers will now be presented with this in view.

THE THEORETICAL, COMPLETE IONIZATION OF TERNARY AND OTHER COMPLEX COMPOUNDS.

156. The student was directed *not to write* the equations for the oxidation-reduction reaction above which involve such ternary compounds as $KMnO_4$, HNO_3, etc. This was because he cannot do this *systematically* until he has learned how such compounds are to be considered in this connection. To simplify the study of their behavior in these reactions, we consider what they would form if they were *completely ionized* into their elemental parts. Thus, the primary ionization of NH_4Cl yields NH_4^* and Cl', but complete ionization into the elemental parts requires the further ionization of NH_4^*. Since 4H* result from this ionization, and thus 3 new (+) charges appear, it follows that 3 (-) have been given up by the H's and these may be written as placed upon the N ion (written $N^{3'}$ or N'''). The whole compound in the form of ions appears as (4H*, $N^{3'}$, Cl'). In the same way the complete ionization of H_2SO_4 requires, after the primary ionization into 2H* and SO_4'', the further ionization of SO_4''. Since 4O'' would result from this secondary ionization, and hence 6 *new* (-) charges appear, six electrons appear to have been obtained from the S, and hence this is written as having six (+) charges on it (written S^{6*}). Hence, sulphuric acid, completely ionized, appears at 2H*, S^{6*}, 4O''.

It is not intended to convey the idea that these ternary substances actually separate before hand or at once into their elemental ions; it is merely intended to express the fact that they may do

so: it is almost certain that *they undergo such ionization* gradually during the progress of an oxidation-reduction reaction.

157. Ascertain whether the italicized elements in the list below when changed from the first to the second compound undergo oxidation or reduction. Express the amount of change in numbers of electrons per atom of the changed element:

	First Compound	Second Compound
(a)	H_2S.	H_2SO_4
(b)	HCl	$KClO_3$
(c)	H_2SO_4	H_2SO_3
(d)	HNO_3	NH_4OH
(c)	$KMnO_4$	$MnSO_4$
(e)	$K_2Cr_2O_7$	$CrCl_3$

NITRIC ACID AND ITS REDUCTION PRODUCTS.

Before the reduction of nitric acid can be discussed it is necessary to acquaint the student with some experimental facts concerning nitric acid. In this connection the student should read, in his text-book, the sections dealing with the commercial preparation of nitric acid, its physical and its chemical properties, and the sections dealing with the preparation and properties of nitric oxide, nitric peroxide, and nitrous oxide.

158. Demonstration of the Great Oxidizing Tendency of Concentrated Nitric Acid.

Secure a porcelain dish, about six or eight inches in diameter, and put into it some tap water. Secure, in a test tube, a few c.c. of fuming nitric and a small piece of charcoal. Hold the test tube with a clamp, warm the nitric acid, and at the same time hold the charcoal, with a pair of tongs, in the flame of a burner until it has ignited. Then, while holding the test-tube over the dish full of water (as a precaution against its breaking!) drop the glowing charcoal into it. The charcoal should burn vigorously in the acid. This shows that nitric acid gives up oxygen quite readily.

159. The Preparation of Nitric Peroxide.

Put a little "scrap" sheet copper into a test tube and add about 1 c.c. of *concentrated nitric acid to it.* The reddish-brown gas evolved is nitric peroxide—NO_2. It is produced by the *least* reduction of nitric acid. Its production under these conditions is all that is to be noted here.

160. The Preparation and Some of the Properties of Nitric Oxide.

Fit up a flask as for the preparation of hydrogen—with a two-hole rubber stopper, a delivery tube, and a thistle-top funnel, the stem of which extends to the bottom of the flask. Put into the flask about 10 grams of small pieces of sheet copper (scrap!), add about 15 c.c. of water, and then when ready for all that is to follow (see below), add gradually an equal volume of concentrated nitric acid. Collect the gas evolved over water. This colorless gas is nitric oxide, NO:—it is only slightly soluble in water. Fill one wide-mouth bottle (about 500 c.c. capacity) wholly with the gas; but fill a second bottle only one-third full and leave this bottle in the water. Then let the gas bubble through a little of a solution of a ferrous salt (use ferrous-ammonium sulphate). The black compound, of ferrous ion and NO, is used as a means of revealing the presence or absence of nitric acid in mixtures, i. e., in qualitative analysis.

Lower a burning match into the bottle full of nitric oxide,—do this with as little loss of the gas as possible. Then lower into the gas a deflagrating spoon with some well-burning red phosphorus. At low temperatures—such as those produced by the burning match even—the nitric oxide does not dissociate sufficiently to furnish oxygen of such concentration as to continue the combustion of the match:—but at the higher temperature produced by the burning of the phosphorus, the dissociation of nitric oxide furnishes oxygen of such concentration as to continue the combustion of phosphorus.

The other bottle, which is filled only one-third full with nitric oxide, is to be tilted so as to admit some air:—note the formation of nitric peroxide which shows that nitric oxide and oxygen combine to form NO_2. Then shake the bottle so as to splash the water up inside of it:—note that the reddish-brown fumes disappear—nitric peroxide dissolves in cold water forming nitric acid and nitrous acid, according to the equation—

$$2NO_2+H_2O=HNO_3+HNO_2$$

This experiment may be repeated until all the nitric oxide has been used up.

161. The Reduction of Nitrates to Ammonia.

Very strong reducing agents (zinc or aluminium) reduce very dilute nitric acid or nitrates to the extreme limit—ammonia. This is most conveniently accomplished as follows:—secure in a test tube some finely divided aluminium, cover it with a concentrated solution of caustic soda, and add a few drops of dilute nitric acid: it will take a few minutes until a vigorous action has set in, then the presence of ammonia will be noticeable.

GENERAL FACTS CONCERNING THE ACTION OF NITRIC ACID WITH VARIOUS REDUCING AGENTS.

162. The nitrogen in nitric acid and in nitrates is in the *highest* state of oxidation in which it ever occurs; and the nitrogen in ammonia or ammonium compounds is in the *lowest* state of oxidation,—it cannot be reduced further. Between these two limits there are a number of oxidation stages, the order and relation of which is shown in the following table. Note that the free element occupies an intermediate position.

TABLE OF NITROGEN COMPOUNDS IN DESCENDING ORDER OF OXIDATION STAGES.

Order.	Elemental Ions from Theoretical Ionization.	Amount of Reduction: Electrons per 1N.
1. HNO_3,—Nitric Acid (and Nitrates)	H^*, N^{5**}, $3O''$	0
2. NO_3, Nitric Peroxide	N^{4**}, $2O''$	1
3. HNO_2, Nitrous Acid (and Nitrites)	H^*, N^{3**}, $2O''$	2
4. NO, Nitric Oxide	N^{**}, O''	3
5. N_2O, Nitrous Oxide	$2N^*$, O''	4
6. N, Nitrogen	N°	5
7. NH_3 (or NH_4OH), Ammonia (or its salts)	N''', $3H^*$	8

The student should commit the foregoing table to memory.

In order to be able to predict what reduction products of nitric acid are likely to be obtained in any one case, the following should be remembered:

163. The *extent of reduction* of nitrogen from nitric acid to a lower oxidation stage depends upon the strength of the reducing agent and the dilution of the nitric acid:—with *concentrated nitric acid*, copper produces NO_2; with dilute nitric acid, copper produces NO, while zinc produces nitrogen; and with *very dilute* nitric acid, *zinc* reduces the nitrogen from nitric acid *to ammonia*. (Note: Nitric acid reacts with all common metals except gold and platinum.)

In attempting to balance oxidation-reduction equations from known facts, certain facts are usually *assumed* to be known: thus, when the reducing agent is a metal, it may be assumed that the student knows that the metal is converted to a salt (metal-ion!); for instance, when copper and nitric acid react, the copper changes to copper nitrate (Cu^{**} ion!). Again it may be assumed to be known that the oxygen ions, *liberated* when an oxidizing agent

such as nitric acid is reduced, will combine with H ions present (to form H_2O).

164. It will now be shown how the known facts in any one "oxidation-reduction" reaction give a definite equation.

Example 1. The Reaction Between Concentrated Nitric Acid and Copper.

The special fact to be known here is that the nitrogen (of nitric acid) is reduced to NO_2. It is *assumed* that the student knows that $Cu(NO_3)_2$ and water are also formed. It follows from the special fact that every HNO_3 reduced requires one electron. Since Cu° in changing to Cu^{**} gives up 2 electrons, it is plain that 1 Cu is oxidized while $2HNO_3$ are reduced. But in this reduction the two HNO_3 also form $2O''$, which require 2H from two other HNO_3 to form $2H_2O$,—thus leaving $2NO_3'$ to couple with the new Cu^{**} ion. All of these relations are expressed by the following equation:

$$\underset{\text{for oxidation}}{Cu+2HNO_3} \quad \underset{\text{extra}}{+2HNO_3}=Cu(NO_3)_2+2NO_2+2H_2O$$

Example 2. The Reaction Between Dilute Nitric Acid and Copper.

In this reaction the nitrogen of the nitric acid is reduced to nitric oxide, NO, hence three electrons are required to reduce one HNO_3: in order that the total number of electrons given up by Cu may be taken up by HNO_3, these must change in the ratio $3Cu:2HNO_3$. Since in this change the $2HNO_3$ form $4O''$ ions, a total of 8 H^* ions, or 6 extra H^* ions are required. All of these relations are expressed by the following equation:

$$\underset{\text{for oxidation}}{3Cu+} \quad 2HNO_3+\underset{\text{"extra"}}{6NHO_3}=Cu(NO_3)_2+4H_2O+2NO$$

Example 3. The Reaction in "Aqua Regia."

When 3 parts of concentrated hydrochloric acid are added to 1 part of concentrated nitric acid, they react to form nitric oxide as the reduction product, and chlorine as the oxidation product. The ratio between the oxidized and the reduced substances is evidently (?)

$$3HCl:HNO_3$$

and the equation is—

$$3HCl+HNO_3=NO+2H_2O+3Cl$$

Example 4. The Oxidation of Ferrous Salts by Dilute Nitric Acid.

Since one Fe** ion gives up one electron to become Fe***, and since nitric oxide is the reduction product formed here from nitric acid, the ratio of the oxidized and the reduced substances is—

$$3FeSO_4 : HNO_3$$

and the equation is—

$$3FeSO_4 + HNO_3 + 3HNO_3 = 3Fe(SO_4)(NO_3) + NO + 2H_2O$$

It is customary to write $Fe_2(SO_4)_3 + Fe(NO_3)_3$ in place of $3Fe(SO_4)(NO_3)$.

Example 5. The Reduction of a Nitrate to Ammonia,—by Means of Aluminium and Sodium Hydroxide.

In the change from nitrate ion to ammonia, each N atom receives 8 electrons; hence the ratio between the Al and the NO_3', which change simultaneously is—

$$8Al : 3NO_3'$$

In the presence of sodium hydroxide, the Al*** ion combines with one Na* and 2O'' ions to form $NaAlO_2$. Each "N" requires 3 H* ions to form NH_3—these H* ions are taken directly or indirectly, first from the NaOH concerned, and the rest of them from H_2O present. Considering all this, we arrive at the following equation—

$$8Al + 3NaNO_3 + 5NaOH + 2H_2O = 8NaAlO_2 + 3NH_3.$$

165. 1. Figure out the equation of the reaction that takes place when copper sulphide is dissolved in dilute nitric acid if at the end the sulphur is present as free sulphur and the nitrogen as nitric oxide.

2. Do the same with bismuth sulphide, and again with silver sulphide.

3. If aqua regia, after its preparation by mixing the acids, is essentially a solution of chlorine (see equation above), what will be the equation for its action upon mercuric sulphide, which results in a solution of mercuric chloride?

4. Note the position of silver, relative to copper, in the table of battery poles, and hence infer what will be the probable reduction product of nitric acid if the concentrated acid reacts with silver. Write the equation for this action.

5. Do the same for lead and dilute nitric acid; and again for cadmium and very dilute nitric acid.

6. State what are likely to be the products formed when hydrogen sulphide is passed into warm, dilute nitric acid, and figure out the equation for the reaction which produces these results.

THE OXIDIZING ACTION OF SULPHURIC ACID.

166. Concentrated sulphuric acid is a powerful oxidizing agent. It is used occasionally just like nitric acid to dissolve copper, silver, or mercury, i. e., metals which do not dissolve in hydrochloric acid or in dilute sulphuric acid by liberating hydrogen gas; and, again like nitric acid, concentrated sulphuric acid does not attack gold or platinum.

Since the main reduction products of sulphuric acid are known to the student, it is advisable to add here the few remarks necessary to inform him concerning the general facts involved in its oxidizing actions.

THE COMPOUNDS OF SULPHUR IN DESCENDING ORDER OF OXIDATION STAGES.

Order	Common Form of Each Oxidation Stage	Theoretical Elemental Ions	Reduction Electrons per S
1	H_2SO_4, Concentrated Sulphuric Acid (and Sulphates)	$2H^*$, S^{6**} $4O''$	0
2	SO_3 (or H_2SO_3), Sulphur dioxide, sulphurous acid, and sulphites	S^{4**}, $2O''$	2
3	S, Sulphur	S^0	6
4	H_2S, Hydrogen sulphide, and other sulphides	$2H^*$, S''	8

Weak reducing agents, such as metallic silver, and metallic copper reduce concentrated sulphuric acid the least amount only—i. e., to SO_2. Strong reducing agents, such as zinc, reduce it to the greatest extent—i. e., to H_2S.

The student should learn the table and these general facts.

167. Put a little "scrap" sheet copper into a test tube, cover it with concentrated sulphuric acid, warm the mixture until reaction ensues:—note the odor of the escaping gas. Repeat this trial with granulated zinc in place of copper.

The equations for these reactions are balanced by considering the data as follows: When sulphuric acid is reduced to sulphur dioxide, two electrons are required per 1S, and if the electrons are furnished by the changing copper, 1Cu must change to Cu^{**} ion (or to copper salt—i. e., sulphate) while $1H_2SO_4$ is reduced. The two O'' ions liberated from $1H_2SO_4$ in its reduction to SO_2 require $4H^*$ ions to form H_2O—hence 1 extra H_2SO_4 is involved in the action. Considering all this, we write—

$$\underset{\text{for oxid.}}{Cu+\quad H_2SO_4}+\underset{\text{extra}}{H_2SO_4}=CuSO_4+SO_2+2H_2O$$

In the same manner the student should balance the equation for the reaction between zinc and concentrated sulphuric acid with hydrogen sulphide as the reduction product.

168. The fact that stronger reducing agents reduce such oxidizing agents as concentrated sulphuric acid to a greater extent than weaker reducing agents is shown well by the action between concentrated sulphuric acid and chlorides, bromides, and iodides, respectively. It is evident from the positions of the latter in the table of battery poles that their tendency to form the free halogens *increases* in the order in which they are here named—chlorides, bromides, iodides—and in accordance with this we find that in the action of concentrated sulphuric acid with chlorides there is no oxidation or reduction, with bromides there is formation of bromine and slight reduction of the sulphuric acid (to SO_2), while with iodides there is formation of iodine and very extensive reduction of the sulphuric acid (to sulphur and to hydrogen sulphide even). For a demonstration, try, in test-tubes, small amounts of potassium iodide and of potassium bromide, respectively, with a little concentrated sulphuric acid. The action between concentrated sulphuric acid and chlorides may be remembered from earlier experiments.

169. With the data indicated in the foregoing, balance the equations which take place in the last two test-tube trials.

THE OXY-HALOGEN COMPOUNDS.

170. The only compounds of the halogens dealt with so far in these oxidation-reduction reactions are the halides—which represent a lower oxidation stage than the free halogens. Besides these, there are other compounds of the halogens, such as chlorates and hypochlorites (bleaching powder!), in which the halogens exist in *higher oxidation stages* than that corresponding to the free halogen, and these are to be considered here.

THE COMMON HALOGEN COMPOUNDS IN DESCENDING ORDER OF OXIDATION STAGES.

(X stands for Cl, Br, or I.)

Order	Common Form of Each Oxidation Stage	Theoretical Elemental Ion	Reduction Electrons per X
1	HXO_4 Perhalate (e. g. perchlorate, $KClO_4$)	H^*, X^{7*} 4O"	0
2	HXO_3 Halate (e. g. chlorate, $KClO_3$)	H^*, X^{5*}, 3O"	2
3	HXO_2 Halite (e. g. chlorite, $KClO_2$)	H^*, X^{3*}, 2O"	4
4	HXO, Hypo-halite (e. g. hypochlorite, KCl O)	H^*, X^*, O"	6
5	Free halogen (e. g. Cl)	X^0	7
6	HX, Halide (e. g. chloride, KCl).	H^*, X'	8

The only oxy-halogen compounds which are of common occurrence are the halates and the hypo-halites—more particularly the chlorates, and the hypo-chlorites. In the formation of these compounds, chlorine, bromine, and iodine are so nearly alike that it is necessary to illustrate with only one of these elements.

The halates (e. g., $KClO_3$) are very stable salts, and strong oxidizing agents. Potassium chlorate is used in many cases where oxidizing agents are needed. In most of these reactions it is reduced to the chloride stage (6 electrons required per $KClO_3$!). The hypo-halites (e. g., bleaching powder), are also strong oxidizing agents, and on this account bleaching powder is one of the most valuable and widely used disinfectants for the purification of potable water, sterilization of sewage, etc. In such reactions, it is mostly reduced to the chloride stage (2 electrons necessary per NaClO).

171. *The commercial preparation* of these substances involves the following reactions:—in neutral or in acidified solutions, the free halogens undergo the following reactions *only to a slight extent:*

$$2Cl+H_2O=HClO+HCl$$

But with strong bases, the corresponding reaction takes place very extensively:

$$2Cl+NaOH=NaClO+NaCl+H_2O$$
$$2Cl+Ca(OH)_2=Ca(ClO)Cl+H_2O$$
$$\text{or } 4Cl+2Ca(OH)_2=CaCl_2+Ca(ClO)_2+2H_2O$$

These reactions present the novel feature that the same sub-

stance acts as the oxidizing and also as the reducing agent: 1Cl is oxidized to the Cl* stage, and another one is reduced to the Cl' stage (ratio 1:1).

(NOTE:—Incidentally the foregoing equations show why chlorine is evolved from bleaching powder when it is acidified:—in the *basic* solution the equilibrium requires that the proportion of the Cl in the form of the *compounds,* chloride and hypochlorite, must be *large;* while in the acidified solution equilibrium requires that the proportion of these compounds to the free chlorine must be *small.*)

172. To 1 c.c. of sodium hydroxide solution add a few drops of bromine water and note how its color disappears (through the formation of NaBr+NaBrO, which are colorless!).

Secure a concentrated clear solution of bleaching powder, test a small amount of it by acidifying the solution with a few drops of dilute hydrochloric acid:—chlorine should be evolved—see explanation above. To another portion add a few drops of a concentrated potassium chloride solution and shake the mixture: crystals of a salt should not separate from the solution. For the application of this, see below.

Boil the remainder of the solution vigorously in a small flask for several minutes, cool the mixture by allowing tap water to flow over the outside of the flask. Test one portion of this cool solution with dilute hydrochloric acid; chlorine should not be formed—at least, not as readily as before. To another portion of this boiled and cooled solution add a little strong potassium chloride solution:—crystals (of potassium chlorate) should appear (see below).

The reaction which ensues in the solution of bleaching powder at the temperature of boiling water results in the formation of chlorate plus chloride, by the *self-oxidation* and self-reduction of the hypochlorite: one Cl passes from Cl* to Cl^{5*} while two other Cl's pass from Cl* to Cl' (ratio 1:2). Hence the equation for this reaction is—

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2$$

The tests made above with this solution depend on the following facts: (1) chlorates and dilute hydrochloric acid react much more slowly than hypochlorites to form chlorine; (2) potassium chlorate is only slightly soluble, while calcium chlorate is very soluble.

In this connection the student should read what his text-book gives on the commercial preparation of these substances, potassium chlorate and bleaching powder. These substances should be used much more freely in the household than they are: a saturated

SUBSTITUTE THIS PAGE FOR ENTIRE ARTICLE 172, ON PAGES 116 AND 117.

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Secure a concentrated clear solution of bleaching powder, test a small amount of it by acidifying the solution with a few drops of dilute hydrochloric acid:—chlorine should be evolved—see explanation above. To another portion add a few drops of a concentrated potassium chloride solution and shake the mixture: crystals of a salt should not separate from the solution. For the application of this, see below.

This reaction between hydrochloric acid and bleaching powder furnishes a very convenient and cheap means of preparing chlorine. Thus, for the purpose for which chlorine is required in Art. 76a, it is merely necessary to put a handful (50 grams) of bleaching powder into the generating flask, and then to allow concentrated hydrochloric acid to drop down upon it.

The Preparation of Halates (Chlorates, Bromates, Iodates).

Halates are always formed from hypohalites, or through the intermediate formation of the latter. This formation of halates is due to the fact that in neutral or *nearly* neutral solutions hypohalites undergo mutual oxidation and reduction. Thus, in the preparation of potassium chlorate given below, 2Cl pass from the hypochlorite to the chloride stage (they are reduced) while *one* Cl passes from the hypochlorite to the chlorate stage (it is oxidized). Hence, with calcium hypochlorite the reaction takes place according to the following equation:

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2$$

To demonstrate the formation of potassium chlorate, mix about 30 grams of bleaching powder with water to make a paste, put a small portion of this mixture into a flask of about 40 c.c. capacity, add a little dilute hydrochloric acid, shake the mixture, dip a stirring rod into it and touch the drop of liquid on the rod to a piece of blue litmus paper: add hydrochloric acid until the mixture turns the litmus paper slightly pink. Then add another small portion of the bleaching powder paste to the mixture in the flask, and acidify this faintly as before. Continue this operation until all the bleaching powder has been treated in this manner. At the end, the liquid should be neutral or faintly alkaline. Boil the mixture for a minute or two in order to hasten the reacting of the last portions of the hypochlorite; clarify the liquid by filtration; and then evaporate it to about one-third its original volume. Then prepare, in a test-tube, a saturated solution of potassium chloride, and mix the clear solution with some of the chlorate solution just prepared: a crystalline precipitate of potassium chlorate will be obtained. If the hypochlorite had not been changed to chlorate would a precipitate have been obtained?

Bleaching powder and potassium chlorate should be used in the household much more freely than they are: a saturated solution of potassium chlorate is a splendid, mild disinfectant for sores,—particularly in the mouth, and hence it is an excellent tooth wash. Bleaching powder should be used freely in cleaning sinks, toilets, etc.

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173. Table of Battery Poles Arranged in Descending Order of Electron Concentrations.

No.	Voltage of each pole coupled with Pole No. 17	Composition of Pole.	Special Notes.
1	−3.2	Potassium metal + Potassium salt solution (N/1 K*)	
2	−2.8	Sodium metal + Sodium salt solution (N/1 Na*)	
3	−2.5	Calcium metal + Calcium salt solution (N/1 Ca**) (Sr, Ba—ditto)	Poles 1-5, inclusive, cannot be constructed as here described, because these metals react with water when they touch it:—these voltages were *calculated* from other experiments.
4	−1.5	Magnesium metal + Magnesium salt solution (N/1 Mg**)	
5	−1.3	Aluminium metal + Alumin. salt solution (N/1 A1***)	
6	−.82	Alkaline solution (N/1 OH′) + Hydrogen gas	See also pole 17.
7	−.76	Zinc metal + Zinc salt solution (N/1 Zn**)	
8	−.55	Solution of sodium sulphide (N/1 S″) + Sulphur	
9	−.43	Iron metal + Ferrous salt solution (N/1 Fe**)	
10	−.40	Cadmium metal + Cadmium salt solution (N/1 Cd**)	
11	−.355	Hydrogen sulphide in water (sat.) + Sulphur	
12	−.34	Lead metal + $PbSO_4$ saturating dil. H_2SO_4 (sp. g. 1.2)	Reaction: $PbSO_4 + 2(-) = Pb^\circ + SO_4''$ Storage cell—neg. Pole.
13	−.20	Tin metal + Tin salt solution (N/1 Sn**)	
14	−.17	Nickel metal + Nickel salt solution (N/1 Ni**)	
15	−.147	Hydrogen Sulphide in N/1 HCl + Sulphur solid	

No.	Voltage of each pole coupled with Pole No. 17	Composition of Pole.	Special notes.
16	−.12	Lead metal + Lead salt solution (N/1 Pb^{**})	Note also Pole 12.
17	0.0	Hydrogen gas + Hydrochloric acid (N/1 H^{*})	See also Pole 6.
18	+.2	Arsenic metal + Arsenic salt solution (N/1 As^{***}) (Ditto for Sb and Bi)	Values questionable. Concentrations not known.
19	+.24	Solid Mercurous chloride (Calomel) + Mercuric chloride (saturated solution)	
20	+.3	Stannous chloride + Stannic chloride	Values questionable, Conc. not known.
21	+.34	Copper metal + Copper salt solution (N/1 Cu^{**})	
22	+.54	Potassium Iodide solution (N/1 I') + Iodine Element (saturated solution)	
23	+.75	Ferrous salt solution + Ferric salt solution	
24	+.80	Silver metal + Silver salt solution (N/1 Ag^{*})	
25	+.86	Mercury metal + Mercurous salt solution (N/1 Hg^{*})	
26	+.88	Sodium Hydroxide solution (N/1 OH') + Oxygen gas	
27	+1.08	Solution of a bromide (N/1 Br') + Free Bromine (saturated solution)	
28	+1.20	NO_2, NO, N, or NH_3 + Nitric acid	Different reduction products according to conc. of acid and strength of reducers.
29	+1.20	SO_2, S, H_2S + Concentrated H_2SO_4	Different products according to strength of reducers.
30	+1.30	Chromic salt solution (Cr^{***}) + Acidified Bichromate solution (Cr^{****})	Reaction: $CrO_4'' + 8H^{*} + 3(-) = Cr^{***} + 4H_2O$.
31	+1.35	Chloride solution (N/1 Cl') + Free Chlorine (saturated solution)	
32	+1.44	$PbSO_4$, solid, saturating dil. H_2SO_4 (sp.g. 1.2) + PbO_2 solid	Reaction: $PbSO_4 + 2H_2O = PbO_2 + SO_4'' + 2(-) + 4H^{*}$
33	+1.51	Manganous salt solution (Mn^{**}) + Acidified Permanganate sol. (Mn^{7*})	Reaction: $MnO^{4'} + 8H^{*} + 5(-) = Mn^{**} + 4H_2O$

No.	Voltage of each pole coupled with Pole No. 17	Composition of Pole.	Special Notes.
34	+1.7	During electrolysis, acidified solutions of sulphates, phosphates, etc., give oxygen gas on platinum anodes at this potential.	
35	+1.9	Solutions of Fluorides (N/1 F′) + Fluorine gas	Not realizable because fluorine and water react on contact.

CHAPTER XIV.

THE PERIODIC SYSTEM.

174. A text-book lesson will be assigned under this heading.

CHAPTER XV.

THE FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY AND THE CHIEF TYPES OF ORGANIC COMPOUNDS.

175. On account of important differences in properties, all carbon compounds (so-called *organic* compounds) are divided into two great classes: the "straight-chain" or *fatty* compounds, and the "cylic" or *aromatic* compounds. The former class includes among other substances the hydrocarbons found in petroleum, the sugars, oils and fats of animal and vegetable origin, etc., and the latter includes the "coal tar" dyes, carbolic acid, naphthalene, i. e., compounds obtained from coal tar or from coal tar distillates. The straight-chain compounds will be presented first, and we will begin with the simplest straight-chain compounds, the saturated hydrocarbons, or the paraffin series of hydrocarbons. They are also called the Methane or Marsh Gas series from the lowest member of the series, which is CH_4, Methane or Marsh gas.

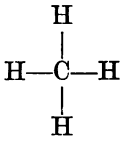
Read what is given in your text on these hydrocarbons and on petroleum.

176. Organic chemistry owes its wonderful development to the *structure theory,* according to which the atoms in organic compounds are tied together by *bonds,* which in number, are equal to the valences of the elements. The special fundamental ideas employed in the structure of carbon compounds are these:

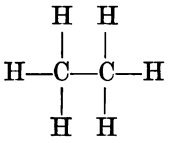
1. The carbon atom always has a valence of 4.
2. A carbon atom may be united to another carbon atom, and this in turn to another and so on without limit.
3. Two carbon atoms may be directly connected by one, two, or even three bonds.

In accordance with these fundamental ideas, the structure of the hydrocarbons of the marsh gas series is represented as follows:

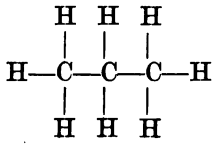
Methane, CH_4



Ethane, C_2H_6



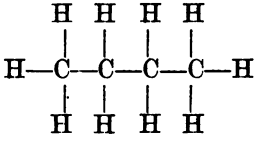
Propane, C_3H_8

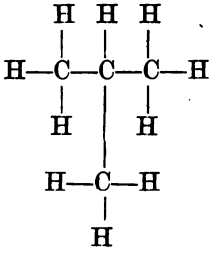


Note (1) that in every instance there are four lines, which represent bonds, or valences, extending out from each C; (2) that in molecules having more than one C, the C's are directly united by bonds.

Since H has one bond only, it is impossible to connect the atoms in the above molecules in any other manner than that shown and still give each carbon four valences.

However, in the following compounds there are several different structural representations possible. Thus with C_4H_{10}, we have either





This theoretical prediction of the existence of two different compounds, both of which have the composition C_4H_{10} agrees with the fact that two such compounds are actually known, and only two are known.

177. Figure out in the same manner how many different compounds with the formula C_5H_{12} are theoretically possible.

178. Chief Property of the Paraffins: Inactivity.

The name *paraffin* is derived from the French and means "no affinity," and it was given to the hydrocarbons of the paraffin series to indicate their chief characteristic. They react with very few reagents, and generally only slowly with any reagents. They are

also called *saturated* hydrocarbons, because they do not *unite directly* with any substance (see unsaturated hydrocarbons). Their marked chemical indifference, or stability, or non-reactivity, makes them specially useful wherever such a property is desired, as in the lubrication of bearings and in the oil wiping of machinery, for either of which purposes vegetable oils are utterly unsuitable. Paraffin is frequently melted into wood and into stone and cement to protect them against moisture (water proofing) and chemical agencies. Thus limestone has been protected in smoky cities (Pittsburg) against the sulphuric acid formed from the sulphur in the coal. The obelisk known as Cleopatra's Needle, in Central Park, New York, has been protected by impregnation with paraffin, and plaster of Paris casts are thus made water proof. In the latter case the objects are painted with a solution of paraffin in benzine or gasoline.

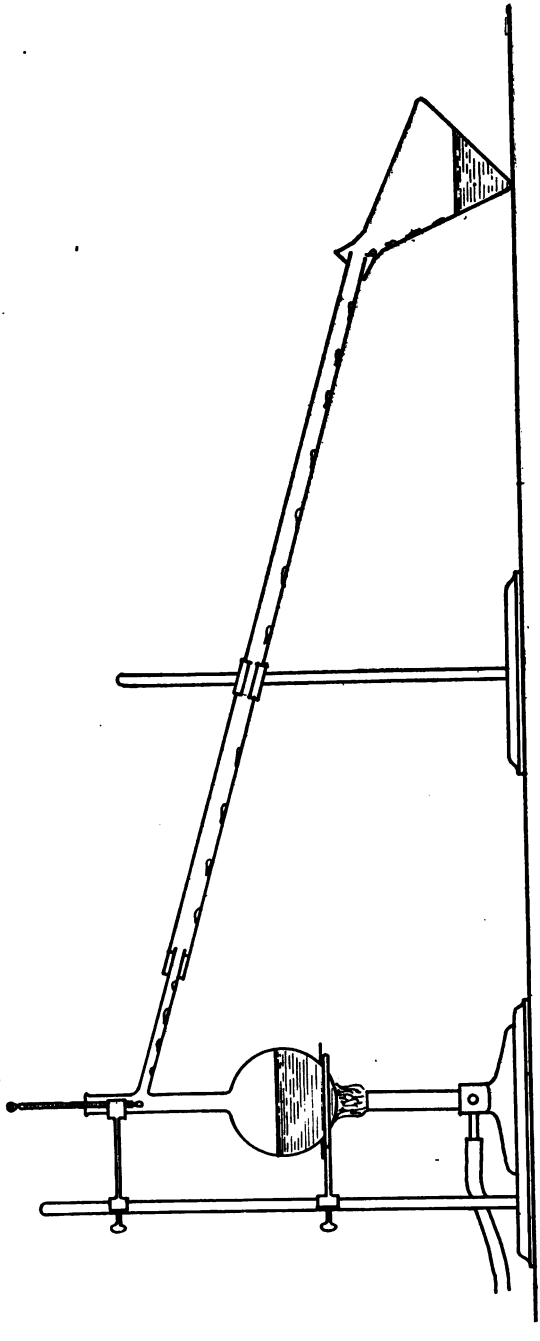
179. The Distillation of Crude Petroleum and the Refining of its Products.

In order to become acquainted with the commercial preparation and the common properties of some of these compounds, distill some crude petroleum (Beaumont oil) and refine the products as follows:

Secure a distilling flask of about 250 c.c. capacity. Fit it with a 360-degree thermometer, and with a wide piece of glass tubing for an "air" cooled condenser (see figure). Secure a piece of asbestos board 6x6 inches and cut a hole in the center two inches in diameter. Place this on the ring of a ring stand, clamp the flask to the ring stand, grasping the flask at the uppermost part of the neck, put any suitable object under the condenser tube for its support, and allow its delivery end to extend into a small flask.

Begin by heating the oil cautiously. If water is present, the upper part of the flask may have to be heated at the same time by a separate flame in order that the water will not condense there. The condenser tube should be placed at such an angle that the condensed liquids will run out quickly. When the temperature has reached 200 degrees, change the receiver and collect the portion coming over between 200 and 300 degrees in a clean, dry flask. Note the odor of the distillates; note the color and contrast it with that of the crude oil. The distillates obtained by two or three students should be poured together to get enough to make a specific gravity determination. If the amount of distillate is too small to use a "hydrometer," then a specific gravity balance should be employed. What is the specific gravity of this distillate? How does it compare with that of the original oil?

180. Each student should then take his portion of the distillate and proceed with it as follows:



Distillation with an Air Condenser

Distillation of Crude Petroleum.

(a) *Removal of Sulphur:* Put a few c.c. of the distillate into a dry test tube, add a little yellow lead oxide, and heat the mixture. A blackening of the solid powder shows the formation of lead sulphide. Sulphur in kerosene, etc., is objectionable because it burns to sulphur dioxide, and is eventually oxidized to sulphuric acid in the air. Commercially, the sulphur is removed by treating the distillate with copper or lead oxide, and then redistilling it.

(b) *Refining:* Put the remainder of the distillate into a dry flask, add one-fifth of its volume of concentrated sulphuric acid, and shake the mixture vigorously. Set it aside until the two portions have separated thoroughly, decant the supernatant liquid into another flask, add distilled water, shake and then decant the oil as completely as possible from the water. Add next some concentrated sodium hydroxide solution, using of it about 5 to 10 per cent of the volume of the oil. Shake as with the sulphuric acid, decant and wash with water as before. The resulting oil should be clear, colorless and of a sweet odor. This treatment removes the tarry matter which colors the oil, and also the small amount of ill-smelling compounds present. Clean all vessels by rinsing them out repeatedly with small quantities of gasoline, and either wiping them dry finally or allowing them to drain until perfectly dry. Reserve a small quantity of the refined oil for use in the experiment below.

The distillates obtained from crude petroleum above 300 degrees are heavier and thicker than kerosene, and are called lubricating oils. The lightest of these are called "spindle oils," the middle grades "machinery oils," and the heaviest "cylinder oils."

At still higher temperatures, vaseline (C_{19} H_{40} to C_{21} H_{44}) is obtained. When paraffin is present in the crude oil, it is extracted from the lubricating oil and vaseline oil distillates by *chilling* these: the solid paraffin separates (crystallizes out) and is filtered off. Crude oils which furnish paraffin are said to have a "paraffin base." In Texas, the Corsicana oils and the Electra Field oils have a paraffin base, but the Beaumont oils have an "asphalt" base, and they yield no paraffin. *Asphalt* is a non-crystallizing, pitchy, or gum-like substance in the oil, which remains in the still until it is completely destroyed, leaving a solid carbon residue. If the distillation is discontinued at 300 degrees C. or slightly above, the residue from *asphaltic* oils forms an excellent *binding* material for road-building. Its value as a road-building material depends upon the per cent of *binder* or asphalt in it, and this is "measured" in a sense by a "pulling" test.

181. In Texas, many refineries do not distill beyond 300 degrees C., and sell the residue for fuel oil.

The purpose for which a lubricating oil can be used depends upon its viscosity, which is readily measured as follows: Take a

25 c.c. or 50 c.c. pipette, and by means of a gummed label mark a point in the stem just below the bulb. Then fill the pipette with water, and note the time required for the pipette to empty from the mark above the bulb to the mark below the bulb. Dry the pipette by warming it above a flame and sucking air through it. Then determine the time required for an oil sample to flow out of this pipette. This period of time, divided by the time required for water to flow out, gives the viscosity. Secure a sample of lubricating oil and measure the viscosity. Then clean the pipette.

182. Flash Point.

Secure a small evaporating dish about 3½ inches in diameter, and a second one a little larger. Put some sand into the larger one, and fit the smaller one within it, so that the two are separated everywhere by a layer of sand. Place these two dishes on the asbestos board with a 2-inch hole in it, fill the inner dish with crude petroleum oil, and suspend a thermometer so that the bulb of the thermometer is immersed in the oil. Heat the oil with an adjustable flame so that the temperature rises uniformly a few degrees (2-4) per minute. By means of another burner apply a very small flame to the surface of the oil once every minute. The temperature with which a flame first flashes across the surface of the oil without continuing to burn is the flash point. At a slightly higher temperature the flame will continue to burn; this is the burning point.

In former years kerosene had to be examined for its flash point, because there was very little sale for gasoline, and hence as much of this as possible was left in the kerosene. At present there is practically no danger from this source, because gasoline is more valuable than kerosene. The flash points of kerosenes found in the Texas markets at present vary from 84 degrees F. to 102 degrees F. In Texas a "minimum" flash point of kerosene is not fixed by law.

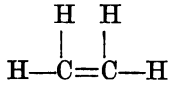
The term *gasoline* is naturally somewhat indefinite. Ordinary "store" gasoline as offered in this market has a specific gravity of 64 to 68 degrees Beaumé (which corresponds to a specific gravity of 0.721 to 0.707). It is well to test the specific gravity of the gasoline because the heavier gasolines are, in general, now less valuable.

Note: The Beaumé specific gravity scale, although very unscientific, is used so much in commerce that a word of explanation will not be out of place here. There are two distinct scales: one for liquids heavier than water and another for liquids lighter than water. The first was designed by dissolving 15 parts of salt in 85 parts of water at 12.5 degrees C. The point to which the spindle sinks in this solution is marked 15 degrees Bé., and the point to which it sinks in water is marked 0 degree Bé. The scale

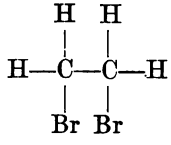
for liquids lighter than water is designed thus: Ten parts of salt are dissolved in 90 parts of water, and the point to which the spindle sinks in this is marked 0 degree Bé., while the point to which it sinks in pure water is marked 10 degrees Bé. Hence on this latter scale the number of degrees increases as the specific gravity decreases, while on the scale for liquids heavier than water the number of degrees increases as the specific gravity decreases.

183. Unsaturated Hydrocarbons.

The two-C member of the paraffin series has the composition C_2H_6, and it has the characteristic property of the paraffin,—namely, of being comparatively non-reactive. There is another two-C compound which occurs in illuminating gas, but which has the composition C_2H_4 and is called ethylene. In order to represent its structure in accordance with the idea that carbon is always tetravalent, we write—

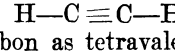


It is very reactive. Thus it combines very quickly with bromine to form a compound of the composition $C_2H_4Br_2$. More bromine than corresponds to this formula is not taken up readily. In order to express the structure of this compound, we write—



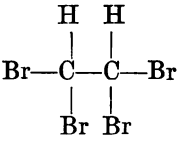
On comparing this with the structural formula of C_2H_4 we note that the second bond between the C's has been broken and the two Br's have been attached by means of the bonds thus made available.

Another two-C compound, which is well known in daily life, has the formula C_2H_2—acetylene. Its structure must be written thus—



in order to represent carbon as tetravalent. This substance takes up bromine or chlorine and many other reagents very readily. With bromine it forms a compound of the formula $C_2H_2Br_4$, but more bromine than corresponds to this formula is not taken up.

That 4Br is the maximum amount that can be taken up is rendered plausible by writing the structure of this compound thus—



which shows that it has a structure similar to the inactive compounds of the paraffin series.

Compounds which like the C_2H_4 and the C_2H_2 above combine readily and directly with other substances are called *unsaturated* compounds: they always show either a double or triple bond in their structural formula. But substances similar to the paraffins in structure do not combine with other substances, and they are hence called saturated compounds. The C's in saturated compounds are connected by single bonds only, in their structural formulae.

184. The above behavior of an unsaturated compound can be readily demonstrated as follows:

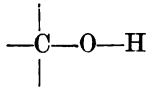
Secure some bromine water; then drop a fragment of calcium carbide into a little distilled water, and pour some of the water, thus saturated with acetylene, into the bromine water until the color of the bromine has disappeared. Acetylene takes up bromine to form $C_2H_2Br_4$. Note how rapidly the reaction takes place.

Acetylene can be burned without the formation of soot if it issues from a very fine opening. Great care must be exercised in handling the gas, because with copper compounds such as may be formed on brass fittings it forms a very explosive carbide, and mixed with air in *any* proportion it forms a very violently exploding mixture. The latter is not true of the other common combustible gases: their mixtures with air are not explosive if either ingredient is present in small amounts. For the above reason, the use of tanks full of compressed acetylene gas cannot be safely used for lighting purposes. But the gas may be compressed into *acetone,* in which liquid it is very soluble. This liquid does not dissolve air or oxygen appreciably and hence contains no explosive mixture. Tanks full of this solution, called "Prestolite," are used for lighting.

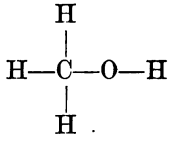
185. Alcohols.

The term *alcohol* is a general one which denotes compounds in which an OH group is attached to a carbon atom with one bond while the other three bonds of this carbon atom are connected to

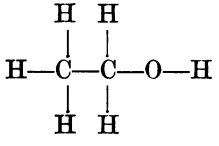
other carbon atoms or to hydrogen atoms. Whenever a compound has this grouping—



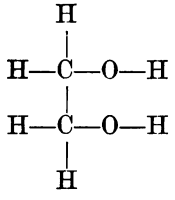
with the three bonds "which are here left open" connected to H or to C atoms, then it is an *alcohol.* Thus the structure of the simplest alcohol in existence, wood alcohol, or methyl alcohol, is written as follows—



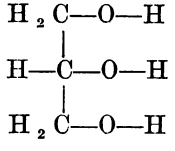
and the compound of the structure—



is also an alcohol (vinous alcohol or ethyl alcohol) because the carbon on the right in the figure shows the characteristic alcohol group. This group can occur on more than one carbon in the compound. Thus glycol $(CH_2OH)_2$ has the structure—



and it is chemically just as much an alcohol as the substances just mentioned above. The same is true of glycerine,



Note the condensed form of the structural formula here given: from now on structural formulae will be written in as condensed a form as is compatible with clearness.

The monovalent radicals (CH_3, C_2H_5, C_3H_7) obtained by taking

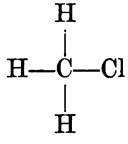
away *one* H from the paraffin hydrocarbons CH_4, C_2H_6, C_3H_8) are named by putting "yl" in place of "ane" in the name of the original hydrocarbon—e. g.:

Methyl, CH_3, is named from methane, CH_4;
Ethyl, C_2H_5, is named from ethane, C_2H_6.

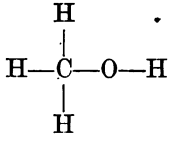
186. The Connection Between Hydrocarbons and Alcohols.

Theoretically the alcohols are the first derivatives obtainable by oxidizing hydrocarbons, but it is practically impossible to make alcohols this way.

For scientific purposes, alcohols have been made direct from hydrocarbons by processes other than direct oxidation, but the process is too expensive to be used commercially. However, this manner of formation of alcohols—direct from their hydrocarbons—is the means by which the structure of the alcohols was recognized—in a manner shown in the following example: by treating methane, CH_4, with chlorine under suitable conditions, a compound of the formula—



is obtained, and if this is treated with moist silver oxide (which may be considered to be AgOH), then by metathetical reaction OH is put in place of Cl, and hence the resulting compound should have the structure—



The compound thus obtained is identical with the compound obtained from the dry distillation of wood, and which is known as wood alcohol, or methyl alcohol. By means of the above scientific preparation of the various alcohols from hydrocarbons, the formulae and structures of the alcohols have been thoroughly proven, and on account of this theoretical relation to the hydrocarbons the alcohols are here considered next in order; however, it should be noted that in their commercial preparation there is no direct connection between the hydrocarbons and the alcohols.

Read in your text-book the portions dealing with the halogen substitution products of the hydrocarbons and the portions dealing with the alcohols. The following is intended to supplement the information there given. Hereafter it is to be understood that

portions of text-books which deal with any of the following topics shall be read when these topics are studied.

187. Properties of Wood Alcohol (or Methyl Alcohol).

Commercial methyl alcohol is often slightly yellowish in color, and has generally a disagreeable odor. Taken internally, it acts as a poison, which, according to its concentration or the quantity taken, will produce severe headaches and nausea, or death. Four ounces taken internally in any form are said to produce either death or permanent blindness in most instances. Even its vapor produces these baneful results, particularly blindness, and hence its use in industry, as a solvent for lacquers or varnishes, and for other uses, is to be deprecated, and the use of vinous alcohol to be advanced. When pure it boils at 66.7 degrees C. and has a specific gravity of .7995 at 15 degrees C. It is perfectly miscible with water, vinous alcohol, and ether; and it is an excellent solvent for fats, oils, resins, and is hence used in varnish making. It is also used as a fuel, and in some cases it is used as a denaturant of vinous alcohol, and it is used to make formalin (which see).

188. The Preparation of Vinous Alcohol by Fermentation.

Secure about 30 grams of glucose or of some cheap molasses, dissolve it in about 150 c.c. of water, add some yeast, shake the mixture thoroughly and warm it slightly (not above 40° C.). Put the mixture into a flask, leave this uncorked, and set it aside in your desk for two or three days, or until the slow evolution of a gas which takes place at first has practically ceased. Secure a piece of ordinary glass tubing about four to five feet long, bend it about four inches from one end—to an angle of about 60 degrees, and fit this short end to the flask with a one-hole stopper. This long tube is to serve as a condenser. Distill about one-third of the fermented liquid and test the distillate for alcohol by the iodoform test below.

189. The Iodoform Test for Ethyl Alcohol.

A qualitative test for ethyl alcohol is made as follows: Warm a little of the solution to be examined, add a few iodine crystals and then add enough sodium hydroxide solution to decolorize the mixture. After the lapse of a short while, a yellow precipitate of iodoform (CHI_3) will appear if alcohol is present in the sample. The reaction may be considered to take place as follows:

$$\begin{array}{l} CH_2OH + 2I + OH \\ | \qquad\quad | \\ CH_3 + 6I + H \end{array} = \begin{array}{l} HCOOH + 2\ HI \\ \overline{\qquad\qquad} \\ CHI_3 + 3\ HI \end{array}$$

or $C_2H_5OH + 8I + H_2O = CHI_3 + 5\ HI + HCOOH.$

Of course, in place of HI and formic acid, their Na salts are obtained. This action is essentially an *oxidation* due to the oxidizing action of the iodine, or, more particularly, of the hypoiodite, NaOI.

Note.—Chloroform is made in the same way, from alcohol, by means of free chlorine gas: the latter is frequently added in the form of chlorinated lime (chloride of lime).

190. Determination of the Per Cent. of Alcohol in a Liquid.

See Allyn, Elementary Applied Chemistry (Ginn and Co.), page 58.

191. Descriptive Data on Vinous Alcohol.

Alcohol and water cannot be completely separated by distillation: at least 4 per cent of water will remain; hence the best commercial alcohol contains about 95 per cent of pure alcohol. The last traces of water can be removed by dehydrating agents only.

Alcohol is found in many substances in commerce. In Texas the legal limit on non-intoxicating liquids is 2 per cent. Beer contains 3 to 5 per cent; sour wines (claret, Sauterns, Rhinewine), 8 to 13 per cent; sweet wines (sherry, port, Madeira), 15 to 20 per cent; brandy, whisky and rum, 45 to 65 per cent. Many patent medicines which are taken in large doses have high per cents of alcohol, and hence their use puts them into the same class with brandy and whisky, etc.: Peruna, 28 per cent; Pain's Celery Compound, 21 per cent; Hostetter's Stomach Bitters, 44.3 per cent. Special mention should be made of the fact that in some cheap extracts, etc., in the preparation of which an alcohol has to be used, as, for instance, in bay rum, Jamaica ginger, Florida water, lemon extract, etc., the poisonous wood alcohol is used instead of vinous alcohol with the consequent danger to the user. Furthermore, it should be noted that in the manufacture of ethyl alcohol by fermentation a number of other substances are formed in greater or lesser amount through the action of ferments different from that which produces ethyl alcohol. Chief among these substances is *fusel oil,* or amyl alcohol, $C_5H_{11}OH$. The formation of this substance can be controlled by proper care in the growth of the ferment, etc., and since the boiling point of the substances in the pure state (132° C.) is much higher than that of ethyl alcohol they may be separated by distillation. Amyl alcohol has a penetrating color. Small quantities of it taken internally produce a stupefying intoxication which is very much worse than that due to pure alcohol, and when taken continuously produce great nervous irritability, dyspepsia, and finally utter ruin of the system. It is contained in cheap, unrefined alcohol, and hence is found in many

patent medicines and cheap alcohol concoctions, which on account of its presence are particularly dangerous.

Ethyl alcohol is one of the most important substances used in industry, e. g., as a *solvent* for gums and resins in making varnishes, lacquers, etc. The amount needed for this purpose is almost inconceivably large. Since it is the least poisonous of all alcohols, its place cannot—should not—be taken by others. The cost of production of this alcohol can possibly be so low that alcohol may even be considered as a possible rival of gasoline for internal combustion engines, and as a rival of kerosene for cooking stoves and for lamps. Alcohol has a decided advantage over kerosene and gasoline because its use as a fuel is attended with less danger and it forms no soot or odor. It can be produced profitably from cheap or refuse grain, potatoes, and even from sawdust. The "Denatured Alcohol Law" passed in June 7, 1906, made it possible to put this material on the market without the payment of the enormous revenue tax. Tax-free alcohol is absolutely necessary for the development of our industries. The price at which it is obtainable at present is still about five times as great as that at which it could be furnished. In order to stimulate the manufacture of denatured alcohol, the U. S. Bureau of Chemistry has built and operated an experimental plant, and has thus determined the cost of such a plant and its operation. The results thus secured, together with directions for denaturing alcohol and all the legal requirements to be complied with in its manufacture, have been published in Bulletin No. 130 of the Bureau of Chemistry, U. S. Department of Agriculture, entitled: "The Manufacture of Denatured Alcohol," by H. W. Wiley. This bulletin is distributed free by the government.

The object of *denaturing* alcohol is to render it unfit for drinking. The denaturant must be repugnant to the taste and intolerable to the stomach—yet it should not be deadly; and it must be so difficult to remove from the alcohol that it will not pay to do it. The main formula for denaturing is: 10 parts of wood alcohol and one-half part of benzine to 100 parts of 90 per cent ethyl alcohol.

192. Ethyl Ether.

Ethers are compounds in which two carbons—one in each of two hydrocarbon radicals—are connected through an O atom—or in other words, by the two bonds of an O atom,—e. g.

H_3 C—O—C—H_3, methyl ether

H_3 H_2 H_2 H_3
C—C—O—C—C, ethyl ether

Ethers are made directly from alcohols: the reaction *appears* as a dehydration merely.

193. Illustration of the Preparation of Ordinary (Ethyl) Ether or Sulphuric Ether.

Put a few c.c. of 95 per cent alcohol into a test tube, insert a thermometer and add gradually an equal volume of concentrated sulphuric acid. Stir the mixture after each addition. Then heat it gently to 145 degrees C., and observe the odor of the vapor issuing from the test tube. This illustrates how ether is manufactured commercially. It *appears* as though the reaction were merely a dehydration of the alcohol.

Ether, just like alcohol, is of great importance industrially—mainly as a solvent for fats, resins, etc., and also as an anesthetic. It has a very low boiling point (34.9° C.) and is very inflammable.

194. Aldehydes.

Aldehydes are the direct products of oxidation of alcohols. The oxygen of the oxidizer acts on the "alcohol" group as indicated in the following equations:

$$\underset{\text{methyl alcohol}}{H_3C{-}O{-}H} + O \rightarrow \underset{\text{formaldehyde}}{H_2C{=}O} + H_2O$$

$$\underset{\text{ethyl alcohol}}{H_3C{-}\overset{H_2}{C}{-}O{-}H} + O \rightarrow \underset{\text{acetaldehyde}}{H_3C{-}\overset{H}{C}{=}O} + H_2O$$

The different aldehydes are named with reference to the acids that they are changed to on further oxidation, which for the above aldehydes are formic acid and acetic acid, respectively.

Aldehydes are prepared, even commercially, by the oxidation of alcohols. For an illustration of this simple action, mix 1 c.c. of ethyl alcohol with an equal volume of dilute sulphuric acid, put into the mixture a pinch or two of powdered potassium bichromate (an oxidizing agent!) and warm the mixture: the acet-aldehyde formed reveals itself by a pungent, slightly sour odor (decidedly different from that of alcohol) and the change of the color of the mixture, from red to green, shows that the chromate has been reduced.

Formaldehyde is now very important in every-day life because its vapor is a powerful poison for bacteria, but not for higher forms of life, and since it penetrates through cloth and into every crevasse, without any injurious effects to fabrics, etc., it is used to disinfect dwellings which have been infected by disease bacteria. It is obtained commercially by the oxidation of wood alcohol. Coil some thin copper wire around a pencil, thus forming a spiral about three inches in length; hold this with the tongs in the tip of

a Bunsen burner flame to oxidize its surface thoroughly, and while hot drop it into a test tube containing 1 c.c. of wood alcohol. Note the sharp odor of the formaldehyde formed. In the commercial preparation, a mixture of wood alcohol and air are brought in contact with hot copper oxide: the copper oxide oxidizes the alcohol, and then the air oxidizes the reduced copper again. Since air alone oxidizes wood alcohol very slowly, the copper oxide acts as a "catalyzer" or hastener of the action. It is now considered that all "catalyzers" are effective through such "intermediate" reaction.

Formaldehyde is found in commerce in the form of a 40 per cent aqueous solution, called formalin. Its wholesale price is about 10 cents a pound, and its retail price should be from 20 to 50 cents, according to quantity. Many methods have been proposed to vaporize the formaldehyde and inject it into a room. The following are the most convenient, the "permanganate" method being slightly less troublesome than the "lime" method, but about twice as expensive:

(a) Permanganate method: For every 1000 cu. ft. of room space to be disinfected, secure 1 pint of formalin and $6\frac{3}{4}$ ounces of permanganate of potash. Close tight all doors and windows of the rooms, spread out over chairs, etc., all bedding and other cloth material so that it will be in as thin layers as possible, open all drawers and cupboards in the room so that the gas may have access to them. Then secure a metal bucket and a large dishpan, place the pan on the floor and the bucket in it, pour the formalin into the bucket, and then pour the permanganate into the liquid in such a manner as to mix them somewhat. The generation of the gas will begin immediately. The room should remain closed for at least 6 to 8 hours. Fine polished furniture should have its flat top covered with a thin cloth to catch a small amount of dust formed by the chemicals.

(b) The lime method: For every 1000 cu. ft. of room space, secure a $\frac{1}{2}$ pint of formalin and $\frac{1}{8}$ pint of concentrated sulphuric acid, and 1 pound of fresh "lump" or quick lime. Place the formalin in an earthenware dish or pitcher, pour the acid into it, and allow the mixture to cool.

Then put the quick lime into a bucket and the bucket into a dishpan, add the formalin-acid mixture, and spread a newspaper lightly over the bucket to catch the "spatterings."

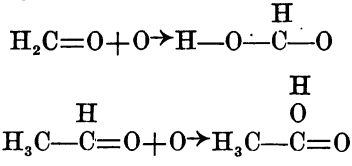
For a demonstration of the above, pour a few c.c. of formalin upon several grams of permanganate crystals.

In the permanganate method the heat evolved by the "burning" up of a part of the formaldehyde to H_2O and CO_2 vaporizes the other part. The lime method makes use of the fact that lime

takes up the water to hydrate itself, and thus leaves the formaldehyde gas without a solvent.

195. Organic Acids.

Oxidizing agents convert aldehydes easily into organic acids. The following equations show the formation and structure of the characteristic acid groups—



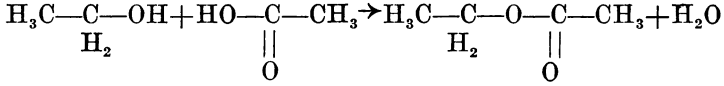
This COOH group (called "carboxyl"), with the fourth valence of the C attached to either H or another C is the essential component of all carbon acids. The simplest example is HCOOH, formic acid; and next to this comes CH_3COOH, acetic acid. The "carboxyl" group may be present more than once in a molecule.

The hydrogen of the COOH group is the "acid" hydrogen.

Acetic acid, which is one of the most important of these acids, is one of the products obtained in the destructive distillation of wood (see Art. 208). It is also obtained by the fermentation of dilute aqueous solutions of vinous alcohol.

196. Esters.

A mixture of ethyl alcohol and acetic acid react slightly according to the following equation:



The new compound is composed of the alcohol radical and the acid radical: it has the C in the alcohol group linked by an O atom to the C in the acid group. Compounds which contain such structures or which are thus made by the joining of alcohol and acid radicals are called esters.

197. Preparation of the Ethyl Ester of Acetic Acid.

Put into a test tube 1 c.c. of ethyl alcohol, add 1 c.c. of glacial acetic acid and then add cautiously 1 c.c. of concentrated sulphuric acid. Shake the mixture and warm it gently,—then note the "fruity" odor. The sulphuric acid here serves merely as a catalytic agent to increase the velocity of the reaction between the alcohol and the acid.

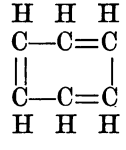
198. Final Suggestions on the Foregoing Types of Compounds.

The theoretical relations pointed out above between the hydrocarbons, alcohols, ethers, aldehydes, acids, and esters, as well as the structures of their characteristic groups should be well memorized because these classes of compounds are of common occurrence and the many different members of these groups have, in general, the same properties—which are really the properties of the characteristic groups, i. e., the alcohol group, the ether group, the aldehyde group, etc. That these groups determine, to a large extent, the properties of their compounds, is true even of compounds with two different groups: the properties of such mixed compounds are in the main the sum of the properties of these groups. Hence it is seen that the study of organic chemistry pursued in the manner shown here is not nearly as laborious as the great number of different compounds possible might lead one to think.

199. The Aromatic, or Cyclic, Series of Carbon Compounds.

All the compounds presented so far may be considered to be derived from the paraffin hydrocarbons, and any one of them might be prepared from any one of the others. The very large group of carbon compounds which are thus related form one of the two main divisions of organic compounds. On account of the theoretical form of the skeleton of carbon compounds, they are called the *open chain* or *straight chain* compounds. The other main division of carbon compounds are called the cyclic compounds because they always contain one or more *rings* of carbon atoms in their molecules. It should be recalled that the open chain compounds are also designated as the fatty compounds, while the cyclic compounds are designated as the aromatic compounds.

The most important carbon ring or cycle found in these "cyclic" compounds is seen in its simplest form in the compound known as *benzene or benzol,* C_6H_6, the theoretical structure of which is written thus:



The figure shows that every C atom is connected with *four* bonds to the other atoms—which is in accordance with one of the fundamental ideas upon which the structure of all carbon compounds is worked out.

These H's which are directly on the benzol ring are easily acted

upon by reagents, and through their reactions other elements or radicals are put in place of one or more of the H's—e. g., C_6H_5Cl, C_6H_5OH, $C_6H_5CH_3$, etc. As may hence be expected there exist many compounds with a benzene ring in their molecules. This benzene ring has decided characteristic properties and it influences the properties of its compounds so largely that all compounds containing a benzene ring have many properties in common.

Besides the *one-ring* nucleus of which benzol is composed, there is a two-ring nucleus, naphthalene, $C_{10}H_8$ and two "three-ring" nuclei, $C_{14}H_{10}$, called anthracene and phenanthrene, with properties similar to benzol, and which together with their compounds are included under "aromatic" compounds.

200. The Commercial Source of the Aromatic Compounds and Their General Properties.

The commercial source of aromatic compounds is the tar obtained in making gas or coke from bituminous coal. This tar, on distillation, yields first an aqueous liquor which contains ammonia, and which is the great commercial source of this substance; and then it yields a series of oil distillates the first part of which (called "light oils") is lighter than water, and is collected separately. It is also known as coal tar naphtha. It contains benzol together with some of its simplest hydrocarbon compounds. When pure, benzol distills at 80.5 degrees C., and has a specific gravity of 0.899 at 0 degree C.

As the application of heat to the tar still is continued and the lower boiling constituents distill out, the temperature rises, and higher boiling constituents pass over. When the specific gravity of the distillate has reached 1, then the receivers are changed; the temperature of the still is then from 170 to 190 degrees C. The next fraction (called "middle oil") is composed of the distillates up to about 230 degrees C. and contains among other substances carbolic acid (C_6H_5OH), and naphthalene. The distillates obtained above 230 degrees C. are called "heavy oils"; they are used wholly or in part for the creosote oil of commerce—for the preservative treatment of timber. Sometimes the portion which distills above 270 degrees C. is collected separately in order to secure the solid *anthracene* which separates from it on cooling. The distillation is either arrested at a temperature between 270 and 300 degrees C., in order that the mass remaining in the still may be used as *soft pitch* (see below), or it may be carried to 340-380 degrees C. in order to secure *hard* pitch.

Properties and uses of the tar distillates: The *light oils* yield mainly benzene and some closely related hydrocarbons.

When the "middle oil" fraction cools, naphthalene separates

from it in crystalline flakes, and may be separated from the oily portion by filtration, etc.

Naphthalene is a powerful germicide, and is used for disinfecting purposes, as well as for the manufacture of some dye stuffs.

The oil filtered from the naphthalene is treated with caustic soda solution to extract the carbolic acid, and the aqueous extract is then acidified, (with H_2SO_4; see the experiment below). Thus the carbolic acid is liberated again, and since it forms a layer of oil on top of the aqueous liquid, it is readily separated from the latter. It is used either in this crude form, or after more refining. The germicidal properties are well known.

The "heavy oils" are composed mainly of chemically *neutral* bodies—i. e., they are neither *acidic* nor *basic*. However, they are all germicidal, a fact which has made them valuable as wood preservers, for which the hydrocarbons of the paraffin series are unsuitable because they are *not* germicidal.

All components of the coal tar oils belong to the aromatic (or cyclic) series of compounds. Hence they all—even the hydrocarbons—react readily with reagents such as nitric acid, sulphuric acid, the halogens, etc., in which reactions the H's directly on the cyclic group are attached and replaced by other elements or radicals. This great reactivity of the cyclic hydrocarbons presents a striking contrast to the non-reactivity which characterizes the straight chain hydrocarbons,—that is the petroleum compounds.

Pitch is an excellent *binder,* and is used as a roofing material (spread on paper, or impregnated with sand and gravel, etc.). "Asphalt paint" is made by dissolving hard pitch in crude benzol or naphtha. The latter evaporates readily, and leaves a smooth coat of pitch. This paint is used to protect iron structures, pipes, sinks, etc. It does not last well on exposure to light and air (it "alligators"), but it does well on material that is frequently repainted, or which is placed in the ground, as water and gas pipes. Such tar or asphalt paint must not contain much free carbon, because the latter tends to stimulate rusting on iron. Raw tar is sometimes used to paint iron, but the ammonia, naphthalene, and possibly other substances present tend to corrode iron, and hence the use of raw tar is inadvisable.

201. Tar Oil for the Preservation of Timber.

The preservative treatment of timber is effected either by injecting a large quantity of an antiseptic liquid into the wood under pressure or by dipping the wood so as to allow the surface to absorb such a liquid. The liquid required for the second procedure must naturally be one which withstands exposure to heat and rain perfectly: hence it should be composed of insoluble oils boiling above 270 degrees C. In neither treatment is it intended

to form a protective coating or to attempt to exclude moisture: moisture can enter or leave such timbers freely, but contact with these fungicidal oils renders it sterile, and thus inhibits the growth of wood-decaying fungi.

A great many steam railroad ties are impregnated under pressure with a solution of zinc chloride. This salt is a fungicide, and preserves ties fairly well in dry countries, though not for as long a time as creosote.

Creosote is an indefinite term which designates vaguely an oil used for wood preservation: it may be anything from the volatile portion of the tar distillates, which would soon evaporate on exposure, to the valuable, permanent high boiling oils. In buying and selling creosote, its quality should be defined by a specification,—or better still, the term creosote oil should be dropped and the term tar oils should be substituted because everybody would realize immediately that the term is indefinite.

It was formerly assumed that the preservative power of the heavy tar oils—creosote—was due to the tar acids and to the naphthalene in it and that certain amounts of these were required to be present in oils used for wood preserving, but recent analyses of well preserved timbers that have been in service for various lengths of time have revealed that the tar acids and naphthalene disappear from preserved timbers fairly soon after treatment (tar acids, by dissolution in water; naphthalene, by vaporization), while the higher boiling oils (particularly those which distill above 270 degrees C.) remain in the timber and preserve it. In explanation of this action of the high boiling oils it should be stated these oils are practically insoluble in water, non-volatile, and yet strongly germicidal. Hence modern specifications call for as low a per cent of tar acids and naphthalene and as high a per cent of high boiling oils as possible.

202. The Production of Wood Preserving Oil.

In Europe all the coke made for use in the production of iron from its ore is prepared in such a way that the tar is saved; and the latter is distilled until the residue forms hard pitch. Hence Europe can furnish an excellent creosote—one containing a large amount of high boiling tar oils. In the United States most of the coking is done without saving the tar; and the tar which is distilled is distilled so as to leave *soft* pitch, because there is a great demand for this material and thus the small amount of creosote prepared in the United States is composed mainly of low boiling oils. It is often made heavier by the addition of some undistilled tar—a procedure which savors strongly of sophistication.

203. Tar Oils: The World's Great Germicides.

Tar oils are largely used as fungicides and germicides, not only in the original state—e. g., as crude carbolic acid, and solid naphthalene, for the disinfection of cesspools, abattoirs, etc.—but also in the form of an aqueous solution. Tar oils dissolve readily in water which contains a sufficient amount of soap. Many proprietary disinfectants, such as "Cresol," "Chloro-Naphtholeum" and similar substances with fanciful names are merely soap solutions of tar oil or of "crude" carbolic acid.

For disinfection these aqueous solutions may be poured or sprinkled into sinks and drains in the original concentrated form, or they may first be diluted with water. In the latter case the oil will separate extensively out of solution, but the milk-like emulsion contains the oil in the form of very small globules. This serves also as an insecticide, in chicken yards, for exterminating flies, etc.

Either the aqueous solution or the creosote oil may be added to sawdust to produce an effective germicidal "sweeping" compound. The commercial sweeping compounds are generally made from the non-germicidal petroleum oils, although these are not as suitable for this purpose.

204. Experiments With Tar Oils.

Set up the same distilling apparatus that was used for the distillation of crude petroleum. Put about 150 c.c. of "creosote for pressure treatment of timber" or crude carbolic acid into the distilling flask, and proceed to distill this as you distilled the crude petroleum. When the thermometer indicates 195 degrees C., put a clean receiving flask on the end of the condensing tube and collect the next 30 c.c. (approximately). Note the final temperature and put another clean receiving flask on the condensing tube and collect about 70 c.c. of the next distillate. Again note the final temperature. The first 30 c.c. will contain a great deal of the carbolic acid in the sample, and will be used to show the extraction of this acid, while the 70 c.c. sample will serve as a fair representative of ordinary heavy oil (creosote) with which some of its properties and uses may be shown.

205. The Extraction of Carbolic Acid.

To the 30 c.c. distillate obtained above, add 20 c.c. of a 20 per cent sodium hydroxide solution, stir the mixture vigorously and heat it to the boiling point; then allow it to cool. By means of a large dropping funnel separate the aqueous from the oily layer. Add another 10 c.c. of sodium hydroxide solution to this oil, stir and heat the mixture and separate it again. Then throw away the oily residue.

Pour the caustic soda extract into a 250 c.c. flask, allow it to cool, add dilute sulphuric acid to it slowly and shake the mixture thoroughly after each addition, and continue the addition of the acid until the mixture reacts acid to litmus. Then add water until the flask is filled well into the neck. Note that an oily layer will collect in the neck of the flask. Observe its odor. By what chemical reactions was it separated from the oil and liberated again?

206. Demonstration of Some Properties of Tar Oils.

Take the 70 c.c. distillate obtained above, cool it to the temperature of the tap water by allowing the latter to run on the outside of the flask and determine the specific gravity of the oil with the specific gravity balance. Note the temperature of the oil while the specific gravity is being measured. In recording this result, state the temperature between which this sample was obtained on distillation and also the temperature at which the specific gravity was taken. Compare this data with the corresponding data on petroleum oils:—the specific gravities of coal tar fractions obtained above 200 degrees C. are always greater than 1.0, while the specific gravities of all petroleum distillates are less 1.0. This fact is used by chemists to ascertain whether or no wood preserving oils are pure tar oils or have been adulterated with crude petroleum.

To contrast the great reactivity of tar oils with the non-reactivity of petroleum oils, put some 20 c.c. of this 70 c.c. sample into a separate small flask and put about 20 c.c. of regular petroleum oil into another flask.

Add four to five times as much concentrated sulphuric acid to each oil, stir the mixtures vigorously and heat them gradually to about 60 degrees, then set them aside for about one-half hour, shaking them at intervals. Next take two large flasks, fill them one-half full of tap water and then pour one of these mixtures gradually into one flask, and the other into the second flask. Finally fill both flasks with water well into the neck and allow them to stand undisturbed for several hours. In the flask containing the petroleum oil almost the whole of the original sample will reappear in the neck, while in the other flask practically none of the tar oil will appear, which shows that the petroleum oils are very slightly attacked by the concentrated sulphuric acid, while the tar oils are completely attacked and converted into water-soluble compounds.

207. The Preparation of Tar Oil Disinfectants and Germicides.

Cut about 25 grams of rosin soap into fine shavings, add an equal weight of distilled water, and warm and stir the mixture until the soap has been dissolved. Then add an equal volume of the remainder of the 70 c.c. tar oil sample, heat and stir the

mixture: a solution of the appearance of black coffee will be obtained.

This solution was referred to in the chapter on colloidal solutions. It has great germicidal power and is found in the trade under such names as chloro-naphtholeum, creoline, etc.

Mix some of this black solution with about fifty times its volume of water:—the mixture will become milk white, will clear up on standing and it will then be found that the tar oil has settled out to the bottom. The surface forces of this dilute soap solution are not able to "dissolve" the oil—hence it separates, at first in very small globules, which give the mixture the milk white appearance.

208. Chemical Products Made by Distillation From Wood and Resins.

To complete the list of chemical manufactures based on the distillation of raw materials, mention should be made of the manufacture of turpentine, rosin, rosin oil, charcoal, wood alcohol, acetic acid, and acetone,—all of which are commercially extremely important and all of which are obtained from wood as the raw material.

The resins obtained by "bleeding" or "boxing" resinous pine and fir trees are mixed with water and the mixture is distilled: the distillate contains a mixture of oils which is commercially known as "gum" turpentine, and the simplest representative of which has the formula $C_{10}H_{16}$. These oils are evidently unsaturated hydrocarbons. The residue left in the retort is the rosin or colophony of commerce.

When rosin is subjected to further—dry—distillation, it yields a distillate called rosin oil, which is used to make axle grease, and it is also used as a cheap (worthless) substitute for linseed oil in paints.

The destructive distillation of non-resinous wood yields the following products:

A. An aqueous distillate called pyroligneous acid, which contains, among other ingredients, acetic acid and wood alcohol.

B. Wood tar, for which there is very little special use, and which is used as fuel mostly.

C. Charcoal, which remains as a residue in the retort.

If the wood is resinous, then it is first mixed with water and distilled so as to secure the turpentine from the resin. This kind of turpentine is called wood turpentine: it has a higher boiling point than the gum turpentine, but is chemically quite similar to the latter.

Distillate A, the pyroligneous acid, has the acid in it neutralized with lime, then the wood alcohol is distilled out of it, and finally the water is evaporated to obtain dry acetate of lime. The latter is used largely to make acetic acid (by treatment with sul-

phuric acid and distillation); calcium acetate is also distilled dry, under which condition it yields a distillate of acetone, $(CH_3)_2CO$, a commercially important liquid, which is formed according to the following equation:

$$\begin{array}{l} CH_3COO \\ \qquad Ca \rightarrow CaCO + CO \\ CH_3COO \end{array} \begin{array}{l} CH_3 \\ | \\ \\ | \\ CH_3 \end{array}$$

CHAPTER XVI.

APPLIED ORGANIC CHEMISTRY: ANIMAL AND VEGETABLE FATS AND OILS, CARBOHYDRATES, AND NITROGENOUS FOOD CONSTITUENTS.

209. Properties and Uses of Some Important Oils of Animal and Vegetable Origin.

The vegetable and the animal fats and oils have the same general composition: they are mixtures of glycerin esters of several "straight-chain" carbon acids. The fatty acids which make up the greater part of these fats have from 16 to 18 C's to the molecule, and only one carboxyl (COOH) group. Glycerin is a trihydroxyl alcohol, $C_3H_5(OH)_3$, hence it reacts with three molecules of the "fatty" acids according to the following equation:

$$3\ RCOOH+C_3H_5(OH)_3=C_3H_5(RCOO)_3+3\ H_2O.$$

Here R represents the rest of the acid molecule except COOH, and is a hydrocarbon radical.

Glycerides of the following acids are found as components of fats and oils:

Saturated acids:

Butyric acid, C_3H_7 COOH
Lauric acid, $C_{11}H_{23}$ COOH
Palmitic acid, $C_{15}H_{31}$ COOH
Stearic acid, $C_{17}H_{35}$ COOH

Unsaturated acids: In all of the following unsaturated acids the hydrocarbon radical contains 17 C, hence if they were saturated the hydrocarbon radical in each one would contain 35 H, as in stearic acid above; the number of H which they have *less than 35* indicates the amount of unsaturation in the acid molecule—

Oleic acid, $C_{17}H_{33}$ COOH, amount of unsaturation, 2H, or one double bond.

Linolic acid, $C_{17}H_{31}$ COOH, amount of unsaturation, 4H, or two double bonds.

Linolenic acid, $C_{17}H_{29}$ COOH, amount of unsaturation, 6H, or three double bonds.

Glycerides of other acids (C_6, C_8, C_{10}, etc.), are also present in some fats.

The glycerides of palmitic acid (palmitin) and of stearic acids (stearin) are white crystalline solids, melting at 61 and 72 degrees C., respectively; that of oleic acid (olein) melts at 14 degrees C., and hence is liquid at ordinary temperatures, and the glycerides of linoleic and of linolenic acids have probably still lower melting

points. The solid fats are composed in large part of stearin or of palmitin or of both, while the liquid oils are composed largely of olein, linolein, etc.

Fresh fats and oils are nearly odorless and neutral in reaction, but when exposed to the air small portions are frequently "hydrolyzed" by the moisture of the atmosphere, and thus a small amount of the free fatty acids and of glycerin are formed. This action is usually *induced* by the fermentation or putrefaction of substances of a gelatinous or albuminous nature which are always present in raw fats and oils, and is accompanied by numerous secondary reactions which produce small amounts of bodies of disagreeable odor and taste. The oil is then said to be rancid. In "refining" vegetable oils, e. g., cotton seed oil, these albuminous bodies are removed and hence the refined oil does not become rancid as readily as unrefined oil.

The fats and oils are specifically lighter than water. They cannot be boiled or distilled, even under *reduced* pressure; heated much above their melting point, they *decompose* into various substances.

The glycerides of the unsaturated acids—particularly those of linoleic and linolenic acids—take up rapidly or react energetically with oxygen, iodine, sulphuric acid, etc. The substances combine with the oil molecules at the double or triple bond, just as HCl combines with ethylene, CH_2CH_2 to form CH_3CH_2Cl, and bromine combines with acetylene to form $CHBr_2CHBr_2$. When oxygen combines with such glycerides at the point of "unsaturation," thick, gummy or resinous masses are formed, which in thin layers become hard, dry, transparent or translucent films, and the change is hence commonly called "drying"—e. g., as in the *drying* of oil paints, etc.

210. The Manufacture and Properties of Cotton Seed Oil.

Cotton seed oil is a mixture of glycerides of fatty acids in which the liquid glycerides (e. g., olein) predominate. It contains approximately 22 to 31 per cent of saturated compounds (mostly palmitin with a little stearin), 59 to 52 per cent of olein (one double bond in each acid radical), and 19 to 16 per cent of linolin (two double bonds in each acid radical). The glyceride of linolinic acid (with three double bonds in the acid radical) is practically absent. On account of the absence of the last named glyceride and the predominance of the *slightly* unsaturated olein, cotton seed oil does not dry to a film as linseed oil does (see below), yet it becomes viscous when it is oxidized (by the air).

211. *The manufacture of cotton seed oil:* Fresh cotton seed is cleaned by passing it first through a screen with a mesh slightly

larger than the seed, and then over a screen with a mesh slightly smaller than the seed: thus, objects both larger and smaller than the seed are removed. It is then *"re-ginned"* to remove the lint, and then *de-hulled.* Finally the meats are crushed between rollers.

The per cents of the different substances thus obtained from the seed are as follows: Hulls, 48.9 per cent; linters, 1.1 per cent; crushed meats, 50 per cent. The latter yields about one-fourth *oil* and three-fourths *meal.*

To prepare the cotton seed meats for the press, the meats are first cooked. The purpose of this is to modify the consistency of the meats through heat so that the oil may be expressed as completely as possible. The heat also expels the excess of moisture and coagulates the albumen. The cooked meats are then molded into cakes to fit the press, and finally the oil is pressed out by means of hydraulic pressure. The cakes taken out of the press are then ground up into the cotton seed meal, which is a valuble feedstuff.

The crude oil is reddish brown in color, and contains impurities. These ferment or putrefy readily and induce the liberation of free fatty acids and other products which make the oil rancid. The amount of free fatty acid in oil is hence an indication of its age, and in commerce its determination is frequently required. Since with the removal of the impurities the tendency for the oil to become rancid becomes much less, this *refining* is undertaken as early as possible. In this operation a certain—variable—amount of oil is lost together with the impurities; hence the value of the crude oil depends on the "refining loss." The determination of the amount of this loss in any particular lot of oil is shown below.

After refining, the oil must be thoroughly dried, first by warming and then by adding plaster of Paris to the oil. This takes up the water as "water of crystallization," forming $CaSO_4$, $2H_2O$. The result is "summer yellow oil."

The yellow oil is bleached by means of fuller's earth: the finely powdered earth is stirred into the oil, and the latter warmed gently. Then the oil is filtered. This gives "summer white oil."

The summer white oil is then chilled and the solid palmitin and stearin (known as cotton seed stearin) separated from the oil by filtration. The clear light-colored oil (known as "winter oil") is extensively used as a salad oil. Except for a slight difference in flavor, it can be used, in cooking, for everything that olive oil can be used for, and it is even more completely digested than olive oil. (The digestion coefficient of cotton oil is 93.5 per cent, while that of olive oil is only 89 per cent.)

212. Products of Cotton Seed Oil: Lard Compound, Cottoline, etc.

Just as a solid and an oily portion may be obtained from the cotton seed oil, so they may be obtained from beef fat (tallow).

These products of beef fat are known as oleo-stearin and oleo-oil, respectively. "Lard-compounds" are mixtures of "summer white cotton seed oil" (which contains all its stearin, etc.), and oleo-stearin. Sometimes lard-stearin is used in place of oleo-stearin. Lard stearin is manufactured from *lard* just as oleo-stearin is obtained from tallow.

Cotton seed oil is also used in making oleomargarin. One formula for making this substance runs as follows:

Oleo oil	495 pounds
Lard	265 pounds
Cotton seed oil (summer yellow)	315 pounds
Milk	255 pounds
Salt	120 pounds
Color	1¼ pounds

These substances are merely mixed mechanically.

Cotton seed oil, particularly those grades which have undesirable flavors or colors, are used to make soap.

213. Methods for the Determination of the Amount of Oil and the Amount of Water in Cotton Seed and Cotton Seed Meal.

At present cotton seed is bought and sold blindly—without any consideration of the quantity and quality of the oil contained in it. The following directions show that determinations suitable for the trade may be made without difficulty even by people who have had but little chemical training. By means of such analyses the buying and selling of cotton seed could be made much more rational than it now is.

214. Determination of the Per Cent of Oil in Cotton Seed—Herty's Method.

In this experiment the non-combustible carbon tetrachloride is used where usually ether, or petrolic ether, are being employed by chemists. The use of carbon tetrachloride makes the operation perfectly safe, while ether makes the operation very dangerous.

Secure about 120 c.c. carbon tetrachloride, and determine its specific gravity, at a definite, known temperature with a pycnometer or with a specific gravity balance. For this purpose the *capacity* of the pycnometer should have been determined previously, or should be determined to begin with. To determine the specific gravity of the carbon tetrachloride, fill either a pycnometer or the cylinder with the plummet belonging to a specific gravity balance with this substance and place the filled vessel into a large beaker filled with tap water and allow it to remain there until the oil and the water may have equalized their temperatures: measure and note the final temperature carefully. Then, if the balance is

being used, weigh the plummet while the cylinder remains in the water; if the pycnometer is being used, secure a short piece of ordinary glass tubing and make out of it a small pipette with a capillary end, and by means of this fill or empty the pycnometer to the holding mark: then take it out of the water, wipe it dry, weigh it, and calculate the specific gravity of the carbon tetrachloride (at what temperature?). The specific gravity at any other temperature may be obtained by *adding* .0018 for every 1 degree C. if this *other temperature is below the original* temperature (or subtracting for every degree above).

Next measure out exactly 100 c.c. of carbon tetrachloride. Then weigh out, in a 200 c.c. Erlenmeyer flask, the samples to be analyzed (i. e., either 40 grams of cotton seed meal or 40 grams of seed previously chopped fine, etc.), warm it in a water bath of approximately 60 degrees C. and then pour the carbon tetrachloride through a funnel upon the sample. Cork the flask loosely, and place it again in the water bath and keep it in there for at least fifteen minutes. Remove it several times to shake it. Then allow it to cool, strain the contents through a wire gauze and pour it upon a folded filter, squeezing the sample on the gauze to remove the liquid as thoroughly as possible. Then determine the specific gravity of the extract in just the same way in which you determined the specific gravity of the carbon tetrachloride. Note the temperature! This determination need not be made at the same temperature as that which the determination with the pure solvent was made. The specific gravity of this extract will be less than that of the solvent alone, because the cotton seed oil has a lesser specific gravity.

Calculate what the specific gravity of the pure solvent would be at the temperature at which the specific gravity of the extract was determined. From this subtract the specific gravity of the extract; divide the difference by .00286. The result is the per cent of oil (if 40 grams of sample were taken!).

Re-distill the extract in order to separate the carbon tetrachloride from the oil. For this purpose secure a water-cooled glass condenser, a 250-c.c. distilling flask and a vessel to be used as a water bath. Carbon tetrachlorine boils at 75.7 degrees C. Return all the carbon tetrachloride to the storeroom. As a substitute for the water-cooled condenser a glass tube five feet long may be used as an air condenser.

215. Determination of the Amount of Moisture in Cotton Seed.

Construct an air bath out of a cheap, two-quart tin can; insert a thermometer through a small hole in the side of the can and fix it in a horizontal position with a little piece of asbestos. Put inside of the can on the bottom a small tin can, or a tea cup, or

anything similar to serve as a support for a four-inch porcelain dish. Put a loose fitting cover over the can.

Weigh out about ten grams of cotton seed accurately and heat this in the air bath at 105 degrees C. until it ceases to lose weight. One to three hours will be required for this. From the loss of weight calculate the per cent of water in the sample.

216. Demonstration of the Refining of Cotton Seed Oil.

The refining of cotton oil has for its object the removal of any free fatty acids that may have been formed (by the action of moisture and ferments) and of the albuminous matter introduced from the seed. It is accomplished by converting the free acids and a little of the oil *into soap.* As the little globules of soap, which are at first spread uniformly throughout the oil,—as they collect and form larger particles and finally settle to the bottom, the mucilaginous impurities are drawn along and collected with this soap.

Secure 5 c.c. of a 10 per cent solution of sodium hydroxide, and also 75 c.c. of raw cotton oil. Put the oil into a small flask or bottle and while shaking the oil gently but constantly, add the sodium hydroxide solution in portions of a few drops at a time. Then warm the mixture by placing the flask in hot water but do not allow it to become so hot that it cannot be held against the skin; continue to stir until the mixture shows a tendency to clarify by the settling out of the soap stock. Allow the latter to settle out thoroughly, decant the clear oil and preserve it for the next operation.

217. Demonstration of the Bleaching of Cotton Oil.

To the refined oil prepared above add approximately three to ten grams of finely powdered fuller's earth. Stir and warm the mixture in hot water and filter it through a dry filter paper. The oil should have become much paler,—if not, the operation should be repeated and possibly a larger quantity of fuller's earth should be used. The action of the fuller's earth is due purely to surface forces.

218. Separation of the Cotton Oil Stearin.

Put into a test tube some of the bleached oil just obtained and cool it in ice water until its temperature is practically at 0 degree C.: those components of the oil which have high melting points will solidify and may be removed by filtration. This solid portion is mostly *palmitin.*

219. The Manufacture of Soap.

The soap stock—fatty material—required for soap making varies according to the kind of soap desired. For white, hard soaps, the best grades of tallow, palm oil, or cocoanut oils are used. Cotton seed oil mixed with tallow or lard also makes an excellent soap stock for white hard soap. A soap stock for hard soaps must contain a large proportion of the non-drying oils (stearin, palmitin, etc.): the sodium salts of these acids are hard, while the sodium salts of drying oils (olein, etc.), are soft like butter, and hence the latter must not be present in too large a proportion in the stock for hard soap.

A good soap should be free of disagreeable odors, free from uncombined caustic soda and also free from uncombined fat; it should be uniform in texture, and should not contain a noticeable amount of foreign substances (filler!). A pure white color also is a good indication of quality.

Perfumes, colors and other materials added to soap as in medicated soaps seldom add anything to the value of the soap, and frequently they are added merely to mislead the public into buying an inferior article or to pay an unnecessarily high price. Pure, good soap is a staple article that can be had at a very low price if bought of the proper source.

Hard soaps are made invariably by means of *soda,* and by "salting" the soap out of the reaction mixture—thus removing the glycerin and other—accidental—by-products. The method of operation is demonstrated below.

In the manufacture of soft soaps, the soap stock is selected so as to contain mostly glycerides of unsaturated acids—e. g., linseed oil, cotton seed oil, etc. Furthermore, these soft soaps are made either by means of *potash,* or, if made with soda, they are not "salted" out, so that they contain the glycerin, etc.

Soap for different purposes and saponaceous compounds, such as pearline, sapolio, etc., are composed of the following substances:

Soft soaps.—Potash soap, together with the whole reaction mixture, i. e., glycerin and water.

Filled or padded soap.—Soda soap with the whole reaction mixture and frequently also impalpable earth powders or water glass (sodium silicate).

Pure, white, hard soaps of best quality.—Nothing but *soap* material carefully prepared so as not to contain an excess of alkali or of free fat (by repeated boiling, with careful adjustment of "stock" to lye). It is heavier than water, but by stirring air into it, it can be made to float on water.

Laundry soap.—Contains, besides soap, an excess of alkali, which is desirable for laundry purposes, but to be avoided for toilet

purposes. The excess of lye is incorporated in the soap by deliberate manipulation.

Yellow soaps.—All yellow soaps are made by using rosin for a part of the soap stock.

Toilet soaps.—(a) Pure, white soap of best quality (see above) is best for a toilet soap. A not undesirable addition is that of some *free oil* or vaseline to the soap: this makes the soap "lather" well.

(b) Medicated or scented soaps are merely ordinary soaps with the drugs or perfumes mechanically incorporated.

(c) Transparent soaps: These are prepared without heating the reaction mixture. This is possible by the use of a readily reacting soap stock—such as castor oil—or by the use of alcohol as a solvent for the fat. The soap contains all the reacting mixture, and usually an extra amount of glycerin is added. The transparency is due to the presence of the glycerin.

(d) Liquid soaps: These are merely dilute aqueous solutions of soap.

Soap powders, sapolio, etc.—These contain gritty earthy substances bound together with a small amount of soap. They usually contain an excess of free alkali.

221. The Determination of the Main Constituents of Soap.

The following exercise is intended to enable students to find out for themselves the chief components of ordinary soap and soap powders, etc.; it is also intended as an illustration of how such work is done. However, students should not mislead themselves into believing that these directions suffice to determine all components, nor to believe that these exercises can make expert analysts out of elementary students:—the exercises merely show something of the methods which a chemist employs in making analyses of such substances as soap.

In this exercise the following components are to be determined:

(a) Insoluble matter,—sand, clay, etc.

(b) Total soap stock (sodium salts of fatty acids).

(c) *Free alkali.*

The amount of *water,* of *undecomposed fat,* and of *glycerin* which may be present are ignored in these determinations. In most commercial soaps, free fat and glycerin are practically absent.

222. The sample to be used should be reduced to fine shavings or to a fine powder. Weigh out in a 250-c.c. flask 10 grams of any white laundry soap or 15 grams of pearline or 25 grams of sapolio. Add 50 c.c. or more of hot distilled water and digest the mass over a mild source of heat until the soap stock seems to

have dissolved. If an insoluble residue remains, *decant* the liquid into a beaker, treat the residue with another, smaller portion of hot water, and if necessary treat it with a third portion of water. Of course the different portions of water are all collected together. The residue, when free from soap stock, is washed into a weighed four-inch dish, the wash water is decanted as completely as possible and the dish and contents are dried by heating them gently over an asbestos board. Weigh the dish and contents and calculate the per cent of insoluble matter in the soap.

223. To determine (b) above, add to the aqueous soap solution exactly 35 c.c. of normal sulphuric acid from a burette, and heat the mixture nearly to the boiling point. Test it with litmus: it should contain an excess of acid, and if necessary, more normal sulphuric acid must be added from the burette. Note the amount added.

The oily layer formed is the free fatty acid obtained from the "real" soap according to the equation:—

$$2R\ COONa + H_2SO_4 = 2R\ COOH + Na_2SO_4$$

The free fatty acids are evidently insoluble in water.

Secure a large dropping funnel—preferably one with an open top—and decant the oily layer into it without spilling any portion of the liquid. When the funnel is full, the aqueous layer is drawn off below and returned to the main portion. By repeating the manipulation, all of the oily layer may be transferred to the funnel. The last drops of the aqueous solution are removed from the funnel by washing with a small amount of water. Some alcohol is then put into the dropping funnel to dissolve the oil, the alcoholic solution is poured into a beaker and the funnel is rinsed out with a little more alcohol, which is added to the other alcoholic solution. A drop of phenolphthalein is added and the mixture is titrated with normal sodium hydroxide.

The number of c. c. of normal sodium hydroxide required by the alcoholic solution is multiplied by .306 and the result is the weight of the real soap in the original sample. Calculate the per cent of soap in the sample.

224. This numerical relation is obtained as follows: one mol. of acid reacts with one mol. of sodium hydroxide, hence the substances are in the ratio—

$$C_{17}H_{31}COONa : NaOH : : 305 : 40$$

(The molecular weight of sodium oleate is 305, that of sodium stearate is 307, hence in our calculation the average value of 306 is used.) But 1 c.c. of normal sodium hydroxide solution contains

.04 gram of solid sodium hydroxide, and this amount forms, by reaction, .306 gram of soap,—as is shown by the above proportion.

225. To determine (c), add a drop of phenolphthalein to the aqueous liquid from which the oil was separated, and titrate this also with normal sodium hydroxide. This determined the *excess* of sulphuric acid used: add the number of c.c. of sodium hydroxide here used together with the number used for the oily layer, and subtract this sum from the total number of c.c. of normal sulphuric acid added to the aqueous liquid: the remainder is the amount of acid used up by *free alkali* present in the soap. Multiply this remainder by .04 to obtain the weight of sodium hydroxide in the soap; then calculate the per cent of the latter present in the soap.

226. The Manufacture and Properties of Linseed Oil.

Linseed oil is obtained from the seeds of the flax plant. When the plants are used for their fiber, they are pulled before the seeds are ripe, and hence the latter, before they are pressed, must be allowed to ripen after being gathered. The seed which has ripened in the field yields the best oil.

The seeds may be pressed cold or hot, or first cold and then again hot. Cold-pressed oil is pale and tasteless, and is used for cooking in Russia. The hot-pressed oil is amber colored or dark yellow.

Linseed oil is the most important of the "drying" oils. It contains a few per cent only of the glycerides of saturated acids (palmitin, etc.), and the remainder is made up of approximately as follows: 5 per cent of olein (one double bond in the acid radical), 15 per cent of linolin (two double bonds in the acid radical) and about 80 per cent of glycerides of acids, the unsaturation of which is equal to three double bonds in each acid radical. It is seen that linseed oil is composed almost entirely of glycerides of highly unsaturated acids which take up oxygen, iodine, etc., readily at the double or triple bonds in their molecules. With the progress of the absorption of oxygen, linseed oil becomes thick, and *in thin films,* changes finally to a dry, hard substance. This change naturally takes place more rapidly at higher temperatures, and hence by "boiling" the oil, and blowing or "stirring in" air during the boiling, it is largely "oxidized," so that such "boiled oil" (frequently called "hard oil") when it is spread out on a surface in a thin film requires only a short time to "dry." The boiling may be carried on to various extents: Thus ordinary "boiled oil" for painting is obtained by "boiling" the oil until it has lost from 8 to 10 per cent of its weight, during which operation its temperature will rise gradually from 130 to

200 degrees C. approximately: or it may be "boiled" until the temperature rises to 260 degrees and even higher. The extent of boiling is determined by the use for which the product is to be used—e. g., as a varnish, or for printers' ink (with lamp black or other pigments), or to make oil cloth or linoleum.

Precaution: Linseed oil spread in thin films reacts so rapidly with oxygen and this reaction gives out so much heat that rags and paper which have been used to clean up paint spots, etc., frequently are ignited from this heat, and, if thrown around promiscuously, may start disastrous fires.

This reaction of linseed oil with oxygen is catalyzed enormously by small amounts of lead or manganese compounds dissolved in the oil. Dilute solutions of lead or manganese rosinate or borate in linseed oil are called *japans* or *dryers,* and when small amounts of one of these is added to raw linseed oil, thin films of the latter will "dry" in about twenty-four hours or so, while films of raw linseed oil without a "drier" will require about three days. Hence a "drier" is added to all paints. This catalyzing influence of lead or manganese compounds is made use of in preparing boiled oil: when a small amount of lead oxide or resinate is added to the oil it need not be heated to as high a temperature to oxidize it rapidly, and hence a lighter colored product is obtained.

Since linseed oil commands a higher price than many other oils, and since no other oil is as well suited as a "pigment binder" in paints, it becomes necessary to test the oil used in paints. For this purpose the determinations of the Maumené number and of the iodine absorption number are best suited because the reactions in these tests involve only the double or triple bonds in the unsaturated acids, and hence "measure" the extent to which the sample has the property of "drying"—which is the *valuable* property of linseed oil.

In the examination of a supposed linseed oil, the specific gravity should also be taken. It is true that different samples of true linseel oil may show considerable variation in the specific gravity and that other oils, such as cotton seed oil, etc., have so nearly the same specific gravity that an admixture of the latter to linseed oil would not be detected, yet with the addition of some other oil, such as rosin oil, which has a considerably different specific gravity, the specific gravity determination reveals the adulteration so readily that it always is advisable to make this test.

227. The Maumene Test.

This is merely an indirect measure of the amount of heat evolved by the reaction between the oil and concentrated sulphuric acid. To make a test, weigh out in a beaker of approximately 150 c.c. capacity, 50 grams of an oil such as cotton seed oil, or 25 grams

of an oil such as linseed oil. Add to the latter 25 grams of kerosene, so that all samples have the same volume. The smaller amount of an oil such as linseed oil is necessary on account of the greater extent of reaction, of the highly unsaturated oils, with sulphuric acid. Surround the beaker loosely with cotton batting and place it inside of a larger beaker, into which it should fit fairly well. Observe the temperature of the oil. Then add gradually from a burette 10 c.c. of concentrated sulphuric acid, and at the same time stir the mixture thoroughly with the thermometer. Continue to stir as long as the temperature rises, and note the highest point at which the thermometer remains constant for any appreciable length of time. The difference between this and the initial temperature is the "rise of temperature." Then clean and dry the beaker, and repeat the experiment with 50 grams (50 c.c.) of water in place of the oil. If 50 grams was the amount of the sample taken, then the Maumené number is obtained by dividing the "rise" obtained with the oil by the "rise" obtained with water and multiply the result by 100. If only 25 grams was the amount of the sample taken and 25 grams of kerosene were added, then a separate extra experiment must be made as follows: take 50 grams of kerosene and determine the rise obtained when 10 c.c. of the concentrated acid are added to it. The Maumené number of the 25-gram sample is then obtained by subtracting one-half of the rise *obtained with kerosene alone* from the rise obtained with the oil sample, multiplying the remainder by 2, dividing this product by the rise obtained with water, and finally multiplying by 100.

In explanation of this test it should be pointed out that this reaction of H_2SO_4 with the acid molecules at the points of unsaturation is evidently one that evolves heat, and the amount of this "heat effect" is, as always, proportional to the amount of reaction product. Since with different pieces of apparatus the same amount of heat (in calories) will raise the temperature of the whole through a different "rise" of temperature, it becomes necessary to determine the amount of rise with a certain amount of heat. For this purpose the determination with water is made, and by dividing the *rise* with water into the *rise* with oil, the results of the determinations are made independent of the apparatus.

228. Demonstration of the Drying of Linseed Oil (Painter's Drying Test).

Secure three small pieces of glass and spread on them with a glass rod as thin a film of oil as possible: use (1) raw linseed oil, (2) boiled linseed oil, and (3) cotton seed oil. Place the slabs in a *nearly vertical* position in your desk. Note the time in days in which the film attains such hardness that the finger does not stick to it when it is touched.

229. An Illustration of the Methods Used in Examining and Distinguishing Between Linseed Oil and Similar Oils.

Linseed oil in paints is frequently adulterated with, or replaced by, corn oil,. cotton oil, fish oil, and rosin oil. The following are some of the most important means used by chemists to distinguish between these oils or to ascertain if they are essentially pure. These methods are mainly quantitative: qualitative tests are of little value because they do not reveal the extent of the adulteration, and slight amounts of adulterations are frequently negligible.

230. The constants to be used here to distinguish between these oils are the following:

Name of Oil.	Specific Gravity at 15° C.	Maumené Number.
Raw linseed oil	.931-.937	103-126° C.
Boiled linseed oil	.936-.938	100°
Fish oil	.927-.933	123-128°
Cotton seed oil	.921-.930	70-90°
Corn oil	.921-.927	70-90°
Rosin oil	.987-1.0	32°

231. Since these constants are the same for fish oil as for linseed oil and since fish oil is a very undesirable oil in paint and should be entirely absent, the following qualitative test is added here in order to aid in its detection: heat a little of the oil nearly to 100 degrees C. and rub a drop of it on the back of the hand,—a fishy odor reveals the presence of fish oil.

232. Rosin oil is another very undesirable, but frequently used, adulterant of linseed oil; surfaces painted with it become "tacky," or "alligator," as it is called, and under the influence of light and air the oil is soon completely destroyed. The quantitative constants given above serve to reveal any extensive adulteration of linseed oil by means of rosin oil, but since it is not always convenient to make such a test the following qualitative test is here added for practical purposes. Warm a little of the oil and add an equal volume of glacial acetic acid. Mix thoroughly and cool the mixture by means of tap water; then add one drop of concentrated sulphuric acid: pure linseed oil gives a sea green color, but when adulterated with rosin oil a violet color shows itself temporarily.

233. Secure a sample of three oils—e. g., of raw linseed oil, of cotton seed oil, and of rosin oil. If desirable the oil from some mixed paint may also be examined: for this purpose allow the paint to settle in a narrow, tall vessel and drain or siphon off some of the supernatant clear oil. If the paint will not settle

readily, dilute some of the oil with carbon tetrachloride, and after separating the clear liquid from the solid, remove the carbon tetrachloride by distillation (save it).

Take the specific gravity of these oil samples and determine their Maumené numbers. By means of this data, decide whether or not the oils are pure.

234. Carbohydrates: Their Mutual Relations and Properties.

The carbohydrates are straight-chain compounds of carbon, hydrogen, and oxygen *only*, in which the hydrogen and oxygen are present in just the ratio to form *water;* hence the name.

Their proximate constituent, into which they may be all resolved more or less directly or readily—is a six-carbon group ($C_6H_{10}O_5$). With reference to this constituent, carbohydrates are thus classified:

(a) *Monosaccharides or glucoses,* $C_6H_{12}O_6$; i. e., $C_6H_{10}O_5+H_2O$. Of these grape sugar and fruit sugar are familiar examples. Five of the carbons have alcohol groupings, and the sixth—an end group—has an aldehyde grouping. Glucoses are usually found in commerce in the form of syrups because they do not crystallize readily. Their sweetness is only three-fifths of that of cane sugar.

(b) *Disaccharides, or saccharoses,* $C_{12}H_{22}O_{11}$; i. e., $2C_6H_{10}O_5+H_2O$. Of these cane sugar and milk sugar are familiar examples.

(c) *Polysaccharides,* $(C_2H_{10}O_5)_n$ This class includes (1) starch and (2) cellulose.

235. In hot acidified solutions, the members of groups (c) and (b) all change to glucose or monosaccharides. This change is undergone quite readily by cane sugar, slowly by starch, and *very slowly* by cellulose. In neutral solutions, all of these substances hydrolyze much more slowly, except at the high temperatures attained under pressure in closed vessels, and which temperature elevation naturally accelerates the change. In alkaline solutions hydrolysis does not take place to any notable extent. On the whole, the carbohydrates may be said to be very resistant to dilute alkaline solutions but readily attacked by dilute acids.

236. To recognize carbohydrates they are "hydrolyzed" to glucose by boiling them in an acidified solution, and then the glucose is tested for by means of *Fehling's* solution. This test depends upon the reduction of cupric salts to cuprous salts, while the aldehyde group on glucose is oxidized. Cane sugar and starch, etc., themselves do not react with Fehling's solution.

237. Make the Fehling's test on a solution of (a) glucose, (b) cane sugar, (c) starch which has been "dissolved" by stirring a little starch into some cold water and then heating the mixture.

To make the test, mix 1 c.c. of copper sulphate solution with 1 c.c. of a solution containing sodium potassium tartrate and caustic soda, using enough of the second solution to dissolve the precipitate of cupric hydroxide first formed; heat this mixture to boiling and add a few drops of the solution to be tested. If monosaccharides are present, a brick-red precipitate will be obtained.

Next *invert* (?) some cane sugar: dissolve a little sugar in water, add a few drops of dilute sulphuric acid, and boil the solution for one to three minutes. Neutralize the acid with sodium hydroxide and test the solution with Fehling's solution! "Hydrolyze" some starch by acidifying the starch solution (?) prepared above and boiling it. It will be necessary to continue the boiling for ten to twenty minutes, because starch hydrolyzes more slowly than cane sugar. Test the solution with Fehling's solution.

Filter paper or cotton are examples of pure cellulose. Try to hydrolyze a sample of cellulose by keeping it in acidified water at 100 degrees: this may be done by placing the container (i. e., a test tube or a flask) in a beaker or other vessel in which water is boiled. After the water in the container is hot, the container may be stoppered to prevent the evaporation of the water in it. After treating the cellulose for two to three hours, test the solution with Fehling's solution.

238. These *hydrolytic* changes of starch or cellulose do not consist of one step only, but of several, and if the change is arrested at different points, different intermediate products may be obtained. Thus starch, which is insoluble may be changed to an intermediate soluble compound, dextrine, which is not yet a monosaccharine because it does not respond to the Fehling test. Similarly, cellulose may be hydrolyzed to intermediate compounds. Of course, when in either case the action is continued long enough, the substance is finally converted to a monosaccharide.

The hydrolysis of starch and of sugar (but not of cellulose, to any practical extent) is also brought about by the action of *enzymes*.

These enzymes may be produced (a) by micro-organisms, such as yeasts and bacteria; (b) by sprouting seeds, etc., e. g., diastase formed in sprouting barley, which hydrolyzes starch to a disaccharide; (c) by special processes of secretion in the higher animals, e. g., ptyalin in saliva.

For the sake of accuracy it should be mentioned that only the monosaccharides are directly "fermentable" into alcohol and carbon dioxide. The action of yeast upon disaccharides is noticeably made up of *two* consecutive actions due to distinct enzymes which are both produced by the yeast plant:

(1) *The inversion of the disaccharides.*

(2) *The change of monosaccharide to alcohol and carbon dioxide.*

In sugar houses the presence of yeast germs must be carefully guarded against by cleanliness. A "sour mill," as it is called, is easily obtained through the fact that the alcoholic fermentation of sugar may be followed immediately by the acetic acid fermentation of the alcohol, because the vegetable organisms which produce these fermentations are frequently carried about by the air. Acetic acid, just as other acids, catalyzes the hydrolysis of disaccharides to monosaccharides. The latter do not "crystallize out" ordinarily as the solutions are concentrated, and by making solutions more viscous they interfere with the crystallizing out of the cane sugar.

NOTE.—This effect of the glucose is made use of in making "pulling candy": the sugar solution is acidified with vinegar and boiled. Thus, as part of the cane sugar is hydrolyzed, a syrup of non-crystallizing glucose is produced out of which even the cane sugar present does not crystallize readily.

239. Effect of Ptyalin Upon the Solubility of Starch.

Make a thick starch paste by mixing a teaspoonful of powdered starch in half a beaker of cold water and then boil for three or four minutes. Cool the starch paste to body temperature and divide it into two portions. To one portion add half a test tube full of saliva. Pour each portion on dry filter papers in two separate funnels, and stand them aside for an hour, collecting the filtrates. Observe that the one to which saliva was added gives the larger amount of filtrate, showing that saliva has made the starch soluble. Test the filtrate for sugar by Fehling's test. The increase in solubility is due to the conversion of starch into dextrine and sugar.

The commercial production of sugar, starch and cellulose from their vegetable sources consists not only of their extraction, but also of their separation from other components of the plants which are extracted with these.

240. The Manufacture of Sugar.

Sugar is obtained from cane by pressing out the juice between rollers, and from beets by "soaking" the sliced beets in water. In either case the liquid contains also some albuminous matter which would ferment readily; it is removed by boiling the solution to coagulate the albumen. A small amount of free acids present is neutralized with lime water, and precipitated, because these calcium salts are insoluble. The liquid, after being freed from the solids, is evaporated to crystallize the sugar.

241. The Manufacture of Starch.

The separation of starch out of corn, potatoes, rice, wheat, etc., requires not only the softening (soaking) and crushing of the

grain, but also the separation of the starch from other matter—usually proteins. (See below.) Some of these are insoluble—for instance, the gluten in wheat—while others are soluble. Besides proteins, oils are present—particularly in the seed germs. The separation of these substances is essentially a mechanical one and consists mainly of extensive kneading of the mass and washing it with a stream of water: the suspended matter usually settles so that the starch forms a separate layer.

To illustrate the above, make a paste of wheat flour and place it in a small cloth bag. Then knead this bag and contents while holding it in a vessel filled with water to collect starch. Finally, to remove the starch as thoroughly as possible from the contents of the bag, continue to knead it under a stream of tap water until no more starch is obtained.

Test the starch with a drop of aqueous iodine (and KI) solution: the deep blue color obtained is characteristic of starch. Test the starch with Fehling's solution to ascertain if glucose is present.

Test the starch water qualitatively for protein. (See below.)

Test the contents of the bag for (a) starch; (b) protein (gluten).

242. The Chemical Properties of Cellulose.

As is indicated in the foregoing, cellulose is particularly resistant to the action of reagents in dilute solutions. This is well illustrated by the fact that cotton and linen goods in cleaning are boiled even in strong soap solutions. Cellulose resists the oxidizing action of chlorine even; hence cotton and linen goods are bleached by means of hypochlorite solutions.

However, cellulose is readily attacked and disintegrated by vapors of acids; or if, after being steeped in dilute acids, it is allowed to dry with the acid on it. In these respects—that is, in its behavior with alkalies, with chlorine, and with acid fumes—it presents a striking contrast to wool, which is readily attacked by alkalies, so that it cannot even be boiled in soap solutions; it is destroyed by chlorine, hence must be bleached by other means (hydrogen peroxide, sulphur dioxide), but it resists acids even when they are evaporated on its surface.

243. The Extraction of Cellulose From Plants and its Preparation for Paper Making.

Although the *woody* or fibrous parts of plants are composed in the main of cellulose, yet they also contain other substances of albuminous, starchy or resinous nature, which are intimately mixed with the cellulose and frequently serve to bind the cellulose fibers together.

Cellulose exists in plants in many different states of hydration.

In the green, growing parts, it is largely present in a more hydrated form than that which corresponds to the formula ($C_6 10_{10} O_5$), while wood contains a great deal in a form less hydrated than that which corresponds to this formula (lignocellulose). The hydrated forms of the green parts of plants are more or less easily attacked by the digestive enzymes and converted to soluble materials (digested!) while cellulose and the lignocellulose are practically not attacked. However, they aid mechanically in the digestion of other components of food.

Pure cellulose may be prepared from plant material as follows: plant material is freed from the hydrated cellulose, from starch and from some of the protein matter by boiling it with dilute acids (1 per cent sulphuric acid or 10 drops of concentrated sulphuric acid to every 100 c.c. of water); then the residue is washed with hot water to remove the acid, and it is boiled in a very dilute sodium hydroxide solution (about 1 c.c. of 20 per cent solution to every 100 c.c. of water): this will remove resins, oily matter, and the remaining protein matter. The residue is washed again with hot water, and finally the last traces of foreign matter—some of which color the material—are removed by oxidation (bleaching!) with chlorine: for this purpose the cellulose is steeped in a small amount of dilute hydrochloric acid to which a very small amount of potassium chlorate has been added. This mixture is heated in a water bath for a few minutes, and afterwards the acid is removed *thoroughly* by washing. The residue may be dried on a clock glass placed on top of a beaker half full of boiling water.

In the analysis of foods and feedstuffs an amount of 1 to 5 grams of the material is weighed, and treated as above stated, to remove the other materials from the cellulose.

In the commercial preparation of cellulose from wood—i. e., for paper—the treatment is usually not nearly as thorough. For the cheapest grades of wrapping paper the fibers are simply torn apart by "grinding" the wood on a grindstone (mechanical pulp!). But for better grades of paper the foreign matter, which glues the fibers together, must be dissolved out by chemical treatment. Only one kind of solution is used in any case.

In most cases this is a solution of bisulphite of calcium and of magnesium. These salts are cheap and very effective. A solution of sodium carbonate, or a solution of sodium sulphate with a little sodium hydroxide are used in some plants. In all cases the boiling takes place in closed vessels under pressure,—hence at as high a temperature as possible so that the chemical actions may go on as rapidly as possible. The wood is put into the boiler in the form of chips.

244. Organic Compounds Which Contain Nitrogen.

None of the organic compounds considered so far contain nitrogen, yet the organic compounds which contain nitrogen are not only large in number, but they are very important, and a certain amount of them in the food of animals and plants is absolutely necessary for their sustenance. The nitrogen compounds in animal and vegetable bodies appear to be derived from ammonia by substitution of one or more of its three H's by carbon groups. According to the basic or acidic nature of the carbon radical, the resulting compound will be more basic or less basic than ammonia, and hence its tendency to salt formation (by addition with an acid, e. g., N H_3, HCl) is either greater or less than that of ammonia. The hydrocarbon radicals of the paraffin series (CH_3, C_2H_5, C_3H_7, etc.), are all strongly basic, and hence their nitrogen compounds are more basic than ammonia (e. g., CH_3 N H_2, C_2 H_5 NH_2, $(CH_3)_3$ N). They are called "amines" and they form salts like this: CH_3 NH_2, HCl called methyl amine hydrochloride. When the "N" is connected to the carboxyl group, which is acidic in character, the compounds are only faintly basic, e. g., $HCO.NH_2$ which is derived from formic acid HCO.OH and is called "formamide." Among the important nitrogen compounds found in animal bodies is urea, $OC(NH_2)_2$ which is sufficiently basic to form a fairly stable salt, OC $(NH_2)_2$, HCl urea hydrochloride. In the vegetable bodies the alkaloids, nicotine, quinine, etc., are the best known nitrogen compounds. They form stable salts with acids.

245. Proteins.

Most of the plant and animal tissues which contain nitrogen are classed together as *proteins*. Proteins also contain sulphur. The per cents of the different elements in protein compounds from various sources range as follows:

Carbon, 51.2 to 54.7 per cent.
Hydrogen, 6.7 to 7.6 per cent.
Nitrogen, 15.2 to 18 per cent.
Oxygen, 20.2 to 23.5 per cent.
Sulphur, 0.3 to 2 per cent.

There is no marked distinction in chemical composition between proteins of plant and of animal origin; yet they frequently have different properties, and they cannot in general be substituted, weight for weight one for the other in food rations, because they are not equally digestible, and, even after digestion, they do not serve equally to replace or build up animal tissues.

Proteins, like carbohydrates, are insoluble in ether, carbon tetrachloride and other special solvents for fats; hence fats may be

readily separated from animal and vegetable tissues without disturbing the other components.

The many different proteins which have been recognized and which have been given special names may be classified as follows:

(a) *Simple proteins,* e. g., albumen, or egg white, gluten in wheat, etc.

(b) *Compound or conjugated proteins,* i. e., combinations of simple protein molecules with molecules of other substances, e. g., casein of milk, which is a phospho-protein.

(c) *Derived proteins,* which correspond to hydrolyzed products of simple proteins; and they are obtainable from either (a) or (b), e. g., peptones, the products formed by the action of pepsin on proteins.

The different proteins differ largely in solubility. Only a few are soluble in water without change (e. g., albumen, a simple proteid, is soluble in water; globulin, also a simple proteid is soluble in a dilute salt solution). These soluble proteins are changed to a coagulated form at higher temperatures (above 65-75 degrees C.); hence they are precipitated when their solutions are boiled. The chemical change produced by this boiling is a slight hydrolysis. Most proteins are soluble in either dilute acids or dilute alkalies, or in both, which dissolution is accompanied by a hydrolytic change in the substance.

If the hydrolytic action is continued, the proteins are finally broken up into soluble substances. For instance, the very insoluble protein called *keratine,* which is the main component of nails, hair, hoofs, horns, etc., may be hydrolyzed into gelatine by boiling water. Gelatine is insoluble in cold water, but soluble in hot water. By long-continued boiling, gelatine finally is hydrolyzed into simpler substances which are soluble in both hot and cold water.

246. This hydrolytic change of proteids, which can be brought about by acids, alkalies and by hot water even is also brought about by enzymes, just as in the case with carbohydrates.

To illustrate: Dissolve a little egg albumen in half a test tube full of water, boil the solution to coagulate the albumen, cool it, add to it about 10 to 15 drops of neutral pepsin solution, then add 3 to 4 drops of dilute hydrochloric acid, shake the mixture and place the test tube in an air bath at a temperature of 38 degrees C. —not higher. Note that the coagulum is gradually dissolved (digested!).

Pepsin is the enzyme found in the gastric juice which, in the presence of hydrochloric acid, hydrolyzes proteins into soluble forms so that they may pass through the walls of the digestive tract into the circulatory system.

247. All proteins, whether in solid or dissolved forms, are colored yellow when heated with nitric acid. To make the test, add a few drops of concentrated nitric acid to a little of the solution or to the solid suspended in water. The addition of an excess of ammonia deepens the color of the solid or of the solution or turns it orange. This is known as the *xanthoproteic* test, and is a convenient qualitative test for proteins.

The Food Value of the Different Food Constituents.

Protein matter is a necessary ingredient of the foods for all animals because their body tissues are composed mainly of protein matter and the broken down body tissues are replaced, for the most part, more or less directly from the protein matter in the food.

The ratio of the digestible non-nitrogenous food ingredients to the digestible protein matter in foods is called the *nutritive ratio.* For the proper feeding of men and animals, the meals should be so designed that the nutritive ratios of all the foodstuffs together have certain values. Thus, for a man with moderate physical exercise, this ratio should be about 5.8; for a man with hard muscular exercise, this ratio should be 6.8; and for one with little exercise, the ratio should be 5.5. These figures have been obtained by the analysis of foods with which men have done well under these conditions. However, men can exist and do fairly well with considerably lesser relative amounts of protein matter in their food. Most meals contain larger rations of protein matter: the extra amount of protein matter serves merely to give heat—just as an equal amount of a carbohydrate would do.

Aside from the requirement of a certain minimum amount of protein matter in foods, the main requirement that foods must fulfill is that they furnish a certain amount of fuel to the maintenance of the temperature of the body. The fuel value of foodstuffs may be calculated by means of Ruebner's factors. These are:

1 pound of protein or of carbohydrates gives 1860 calories;
1 pound of any animal or vegetable fat gives 4220 calories.

This means that these substances, when burned to water and carbon dioxide, evolve this much heat. It is possible to estimate the fuel value of foods from these figures because the digested—assimilated—portions of food are converted almost entirely to water and carbon dioxide.

The fuel value of a food may be said to be the most direct measure of its value.

Ascertain the analysis of any particular foodstuffs—say, of oatmeal—and calculate its fuel value.

Since men determine the quantity of food eaten by the bulk of

the food, it becomes advisable to choose foods in different seasons or climates so that *roughly equal* volumes have greater or lesser fuel values as the weather, climate, or the occupation of the individual may require.

The daily rations of men have been given by one authority (Atwater) to be such as to have the following fuel values:

For a man with light muscular exercise, 2800 calories.
For a man with moderate muscular exercise, 3500 calories.
For a man with light muscular exercise, 4060 calories.
For a man with hard muscular exercise, 5700 calories.

248. Optional Exercise: The Determination of the Amount of Protein Matter in Food or Feed Stuffs.

See *Allyn,* Elementary Applied Chemistry, page 113.

249. The Composition of Food and Feed Stuffs.

Food and feedstuffs are ordinarily considered as made up of the following six "proximate" components: water, ash, fats, carbohydrates, protein, and crude fiber. In Texas every bag of feedstuff must be tagged with a label which states the per cents of these components present in the contents, as determined by the State Chemist, at College Station. The analysis of a foodstuff should report the same constituents.

Vegetable foods furnish some protein. Wheat has a larger per cent of protein than any other cereal. It contains from 10 to 18 per cent of protein (gluten) and from 65 to 70 per cent of carbohydrates exclusive of fiber. Animal foods, with the exception of milk, furnish practically no carbohydrates. Milk furnishes all essential food constituents. Since this substance is such a frequently used article of diet, a demonstration of its components is desirable.

250. Determine the specific gravity of milk: that of fresh milk is between 1.029 and 1.034, while that of skimmed milk is higher.

Determine the amount of butter fat present, by Babcock's method:

Pipette off 17.6 c.c. of the carefully mixed sample into a test bottle and add 17.5 c.c. of commercial sulphuric acid (specific gravity, 1.82 to 1.83). Mix, and when the curd is dissolved, whirl the test bottles in the centrifuge for four minutes at the required speed for the machine used. Add boiling hot water, filling to the neck of the bottles, and whirl for one minute; again add boiling water so as to bring the fat within the scale on the neck of the bottles, and after whirling for one minute more read the length of the fat column, care being taken to make the readings at a temperature between 130 and 150 degrees F., when the fat is wholly liquid. The readings give the per cent of fat in the milk direct.

In Texas milk must have at least 3.5 per cent of butter fat to be considered unadulterated.

Caseinogen is the chief proteid of milk. To separate it from the liquid, saturate milk with some neutral salt, such as sodium chloride or magnesium sulphate. The caseinogen and the fats will be precipitated together. Filter, saving both precipitate and filtrate.

Dissolve the precipitate in clear lime water or in a very dilute sodium hydroxide solution. Heat the solution so that the fats will melt and float on top, and then neutralize the alkali cautionsly with acetic acid: the protein will be precipitated again.

Milk also contains *albumen*. This will be found in the filtrate obtained above. Heat this to precipitate the albumen. This is the substance that forms the *skin* when milk is boiled.

Finally demonstrate the presence of milk sugar by testing the same liquid with Fehling's solution.

251. Some Chemical Properties of Fibres: Cotton, Wool, Silk.

The properties of cotton (cellulose) and of wool (protein: keratine) have been given above. Silk is a nitrogenous animal fibre with properties somewhat different from those of wool. It contains no sulphur. It is not quite as easily attacked by alkalies or by chlorine as wool, but it will dissolve in strong caustic alkali solutions as wool does. Dilute acids do not affect it as they affect cellulose. True silk may be readily distinguished from artificial silk, because the latter is merely cellulose in composition and properties.

The simplest way to distinguish between cotton on one hand and silk and wool on the other is to try to burn the material: if it burns readily after ignition, and gives out no particular odor, and leaves a white ash, it is cotton. Silk and wood do not continue to burn readily after ignition, the burning of wool produces a decided odor (of ammonia, etc.), the burning of silk produces a similar, but fainter, odor, and these animal fibres leave a crisp coal. Confirm these facts by using pure samples of the fibres.

Woolen fibres can be recognized under the microscope by the scales on their surfaces. Silk and cotton fibres have smooth surfaces. The cotton fibre appears as being very much twisted. Samples of the different fibres should be examined under a microscope.

Secure samples, of about one gram each, of white silk, white wool, and white cotton (yarn or cloth). Place these samples in small beakers, cover them with a ten per cent solution of sodium hydroxide, and stir the mixture so that the solution may act thoroughly on the fibres: the cotton will remain undissolved, but the silk and the wool will dissolve. To the solutions of the latter, add a

little lead acetate: the wool solution will give a precipitate of lead sulphide, but the silk solution should give none.

Secure a piece of cloth composed of both wool and cotton, and dissolve out the wool by means of a ten per cent solution of sodium hydroxide.

Silk can be separated from wool and cotton by means of a solution of zinc chloride which is so concentrated that it has a specific gravity of 1.70, and in which some zinc oxide has also been dissolved.

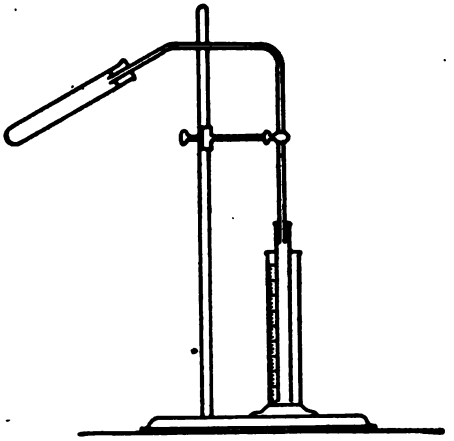
Wool must frequently be freed from burs and from seeds, or even from cotton: for this purpose, it is steeped in dilute hydrochloric acid, or in dilute sulphuric acid, and then allowed to dry partly. On drying, the dilute acid attacks and disintegrates the cellulose (cotton, burs, etc.), but does not affect either wool or silk appreciably. For a demonstration, secure a bit of cotton cloth, steep it in some dilute hydrochloric acid, squeeze out the excess of acid and lay the cloth aside to dry: when dry, it will be found to easily disintegrated mechanically.

CHAPTER XVII.

SIMPLE EXPERIMENTS FOR ILLUSTRATING THE VOLUME RELATIONS OF REACTING GASES AND A SIMPLE ILLUSTRATION OF HOW MOLECULAR WEIGHTS WERE ASCERTAINED.

252. To Demonstrate the Ratio by Volume Between Oxygen and the Sulphur Dioxide Formed From It.

The apparatus to be used in this experiment is shown in the accompanying figure. Some heavy petroleum or lubricating oil is poured into the measuring cylinder; the test tube is detached and filled with oxygen (by displacement of air) and a little piece of roll sulphur is dropped into it. It is then attached again. Some of the oil is now drawn out of the cylinder so that, when the



enclosed gas expands later on the oil will not flow over the top of the cylinder. Note where the level of the oil is within the tube, then heat the sulphur cautiously: when the sulphur burns, the enclosed gases will expand, but on cooling they will contract until the level of the oil is again at the place at which it was before the sulphur was burned. This shows that sulphur dioxide occupies the same volume as the oxygen from which it is formed.

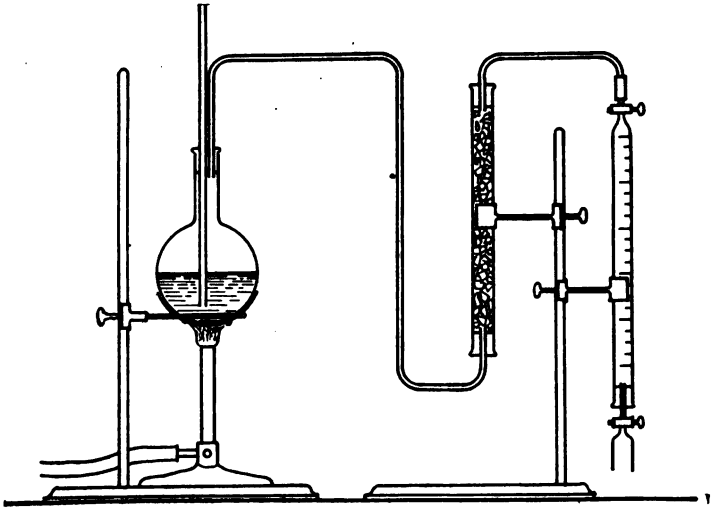
253. To Demonstrate the Ratio by Volume in Which Oxygen and Nitric Oxide React.

One student out of ten should set up the apparatus for the preparation of nitric oxide, while another *one out of ten* sets up

the apparatus for the preparation of oxygen. Each student should fill, over water in a large pan, a test-tube nearly full (not quite full) with nitric oxide gas, and another test tube nearly full of oxygen gas. Mark, with rubber bands, the position of the surface of the water in both test-tubes. Then transfer a small amount of the nitric oxide to the oxygen test-tube, by tilting the former with its mouth under the latter. Nitric peroxide will be formed immediately, but will dissolve in the water gradually. The whole of the nitric oxide should be transferred gradually to the oxygen test-tube. When the colored gas has been absorbed by the water, and the level of the latter does not rise any more, mark this final position of the water with another rubber band. Empty the tubes, and, by means of water drawn from a burette, measure the volume of the nitric oxide used, and of the oxygen used (not the volume of the remaining oxygen!). The ratio by volume in which nitric oxide reacts with oxygen will thus be found to be 2:1.

254. To Demonstrate the Ratio by Volume Between Ammonia Gas and the Nitrogen Obtained From It.

The apparatus to be used is shown in the accompanying figure. An ordinary burette is used and its end is closed by a rubber stopper through which a dropping funnel has been inserted. The



burette is filled with dry ammonia, generated by boiling a concentrated solution of ammonia and passing the gas through a drying tower filled with fresh quick lime. The gas should be passed

in *at the top* of the tower, and again in *at the top* of the burette. Note that the figure is not correct in this respect. When enough ammonia has passed through the apparatus and burette to have swept out all the air, then the stop cocks at the ends of the burette tube are closed. 50 to 100 c.c of a concentrated solution of chloride of lime is then prepared and poured cautiously through the funnel into the burette, care being taken that no air enters the burette. When no more of the liquid is drawn into the tube the stop cock is closed and the burette is laid aside until it has cooled down to the temperature of the room. Then the lower stop cock is opened *while this end is under water;* thus the pressure within the burette is made practically the same as the atmospheric pressure. It is then seen that the nitrogen in the tube occupies just one-half the volume occupied by the ammonia from which it was formed. The chlorine in the chloride of lime combined with the hydrogen of the ammonia and left the nitrogen free.

255. These experiments show that the *volume relations* of reacting gases are *extremely simple.* The fact that this simplicity exists in the volume relations of *all* reacting gases was first recognized and pointed out by Gay Lussac, and hence is known as the *law of Gay Lussac.* This simplicity in the behavior of gases, together with two other similar examples of extreme simplicity in the behavior of gases—namely, their change of volume with pressure and with temperature (the *laws of Boyle* and of *Charles,* respectively), these three simplicities in the behavior of gases led Avogadro, an Italian physicist, to ponder concerning a possible similarity of structure of all gases which would render these simplicities *plausible;* and thus he was led to the opinion that "equal volumes of all gases at the same temperature and pressures contain the same number of molecules."

256. If Avogadro's idea is correct, then the *weights of single molecules* of two gases,—e. g., of nitrogen and of ammonia—are in the same ratio as the weights of equal *volumes* of these gases (both under the same pressure and temperature). But the ratio of the weight of a liter of ammonia to the weight of a liter of nitrogen is 1 : 1.65 (both being at the same temperature and pressure). If now, we knew the weight of a molecule of nitrogen, we could calculate the weight of a molecule of ammonia with this ratio. The weight of a molecule of nitrogen *can be* obtained by considering the facts in the last experiment above, thus:

257. If the whole burette full of gas contains "a" molecules, then one-half of this burette full of a gas contains "a/2" molecule (according to Avogrado) and since each one of the "a" molecules of ammonia contains at least one atom of nitrogen, then there must

be at least "a" *atoms* of nitrogen in "a/2" *molecules* of nitrogen,—hence at least 2 *atoms* in each *molecule* of nitrogen. Since in our system of relative combining weights, or atomic weights, an atom of nitrogen has a weight of 14 units, it follows that the *molecule* of nitrogen must have a weight of 28 units.

258. Having thus obtained the weight of the molecule of nitrogen, we calculate the weight of ammonia by this following proportion:

$$28 : x : : 1.65 : 1$$
$$x = 17$$

this number, 17, is the same as the number indicated by the formula—as it should be.

From now on we can obtain the molecular weight of any other gas simply by comparing the weight of any certain volume of such a gas with the weight of an equal volume of nitrogen (under the same conditions); and then making the same calculation that has just been made above.

259. It should be emphasized that, although according to this illustration, the *first* molecular weight obtained is that of nitrogen, yet when this first step in ascertaining molecular weights was taken years ago, a *number of experiments* similar to the last one given above were considered, and the molecular weights of a number of elements were obtained by means of the same argument that was employed for nitrogen above; and the molecular weights of other substances obtained by comparison with any other element are the same as those obtained by comparison with nitrogen. In practice, molecular weights are obtained by comparison with oxygen mostly.

Finally, it should be mentioned that most elements in the gaseous state have two atoms in the molecule, but some few have more and some only one atom in the molecule.

TEACHER'S MANUAL

FOR A COURSE OF LESSONS
AND EXERCISES IN

GENERAL CHEMISTRY

PREFATORY NOTE.

The following pages present a discussion of the planning and conducting of a course in general chemistry, and give definite directions for conducting a course according to Part II of this bulletin: A Course of Lessons and Exercises in General Chemistry. These two parts, together with Part I on Equipment, form the complete bulletin which is intended to aid high schools and colleges in Texas in designing their courses in general chemistry. Part I has been issued earlier,—as Bulletin 329. It gives definite directions and estimates for equipping a laboratory for this work. A supplementary list of apparatus and chemicals is given at the end of this Part III: this list must be added to the list in Part I in order to complete the list of supplies necessary for the exercises given in Part II.

Part II, the student's manual, has also been issued separately, by the author, for class use.

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CHEMISTRY IN THE HIGH SCHOOL: PART III.

TEACHER'S MANUAL FOR A COURSE OF LESSONS AND EXERCISES IN GENERAL CHEMISTRY.

INTRODUCTION: FUNDAMENTAL CONSIDERATIONS FOR THE SELECTION OF THE TOPICS FOR A COURSE IN GENERAL CHEMISTRY.

Since only a small per cent of students who take courses in general chemistry pursue the subject farther in college, these general courses should be designed primarily for the students who will *not continue* the study of chemistry beyond such a course. Fortunately, courses may be designed so as to suit both this class of students and also the class of students who intend to continue the subject as a specialty. It is intended here to show how this may be done.

Every school course must fulfill three requirements. First, it must give mental training; second, it must present the subject systematically—that is, it must facilitate the further study of the subject; third, it must interest the student in the subject—which is done usually by showing him what use he may make of what he has learned. The topics for a course in chemistry must be selected so as to meet all three of these requirements; to attempt to attain only one of these will produce a course of much less value. By selecting topics from the domains of pure and of applied chemistry, a course may be obtained which fulfills all three of these requirements. It should be emphasized that both pure and applied chemistry are necessary to attain the object sought.

When courses in general chemistry were first introduced in the schools of the United States, the importance of chemistry in commerce and manufactures probably impelled its introduction into the curriculum as much then as it does today, and attracted many students to the study of this subject. But a recent investigation has shown a steady decrease, during the decade from 1900 to 1910 in the per cent of high school students studying the subject. Many teachers consider that this decrease is due to the slight attention—not to say inattention—given to applied chemistry; hence at present teachers of general chemistry are making a special effort to improve their courses in this respect.

As judged by some recent text-books, this effort to teach applied chemistry tends toward a neglect of pure chemistry with its consequent baneful effect on the course as a whole. If the present

revision of the general chemistry courses is to be productive of permanent good, then special care must be taken to give both pure and applied chemistry adequate consideration.

This is a difficult problem, and is made more difficult by the fact that an essential part of organic chemistry must be included in the course, because in our daily life we have as much to do with the compounds of carbon as with the so-called inorganic compounds.

It would evidently be a mistake to attempt to solve this problem by touching the whole surface of the subject, "skimming over it" in a sense; a better solution consists of selecting a relatively small number of important topics and treating them adequately. This is the fundamental idea with which the topics in this book have been selected and treated. A list of these topics is given below, together with the reasons for selecting them.

LIST OF TOPICS FOR A GENERAL COURSE IN CHEMISTRY AND REASONS FOR SELECTING THEM.

Introductory chapters which present experimental examples for the general demonstration of changes, the influence of heat, what is meant by solution, general exercises in weighing, measuring, etc., are of questionable value. At best they are rather unfruitful and uninteresting to the student. Hence they have been omitted in this course. Care has also been taken to avoid beginning by giving definitions, for instance, of *elements, compounds, chemistry, atoms, molecules,* etc. Starting with the definitions reverses the attitude of the student toward the subject matter, and it is really contrary to the natural method of learning a new subject. We teach a child a new thing by showing this thing, and mentioning its name and perhaps speaking about it. This should be the method of procedure in the introduction of this subject.

The course opens with some of the usual experiments given in the chapters on oxygen, hydrogen, and water, for the purpose of presenting the relations of compounds to elements, the quantitative relation shown by substances undergoing very simple chemical changes, such as *decomposition,* hydration, etc. The quantitative significance, and the use, of symbols is taught without reference to atoms and molecules; and the conditions which affect all tendencies to chemical reactions (i. e., temperature and concentration) are pointed out.

After the first few lessons have been given without involving the notions of atoms and molecules, the latter are then to be introduced. But this presentation should be limited to a consideration of the atomic theory, and no mention should be made of Avogadro's hypothesis nor of molecular weight determinations. Mole-

cules are to be considered only as groups formed by the union of atoms.

Toward the end of the course Avogadro's hypothesis and the molecular theory may be studied, but here again a word of caution is necessary: the subject should not be studied unless some essential experimental facts are presented,—that is, some of the experiments which form the basis of these theoretical considerations must be actually performed by the students. In order that the teacher may not lose time in securing simple, easily performed experiments for this purpose, suitable experiments have been given in this book.

The fundamental idea in the arrangement of the subject matter beyond this general introduction just discussed is the following: direct the student's attention to one simple type of reaction and enable him to learn this thoroughly before introducing to him any examples of another type.

In the arrangement of subjects found in most text-books neither the general types of reactions nor any classification according to the most prominent chemical properties of the substances have been considered. Thus, nitrogen and its compounds are invariably presented very early in the course, although the reactions between nitric acid and metals are always complex. They involve not only the simple reactions of hydration and double decomposition, but they also involve oxidation and reduction, and hence they should really be placed at a point farther on in the course. Again, many *simple* reactions which are presented by the interaction of salts of metals with common reagents, such as silver nitrate with hydrochloric acid, ferric chloride with sodium hydroxide, etc., are usually given at the end of the course, and yet they are the simplest kinds of chemical changes. As a result of the constant mixing up of all kinds of changes from the very beginning of the course, the student generally fails to grasp the fundamental principles in any, and instead of learning the properties of elements and compounds in their proper relation, that is, each as an example of a *general* fact, he tries to learn them all as isolated *specific* properties.

During the last thirty years our knowledge of reactions in aqueous solutions has increased so much that we may now be certain of the fundamental facts concerning them: it is definitely known that metathetical reactions depend upon the degree of ionic dissociation, while reactions involving oxidation and reduction depend upon additional facts, namely, those learned in the study of the galvanic batteries. The study of chemistry is immensely simplified by the application of this knowledge and a course arranged to set forth clearly these two fundamental types of chemical changes will enable the student to get a grasp of the chemically important properties of substances which is otherwise

not so easily obtained. For this reason the material is arranged here so as to present at first only substances which undergo mainly metathetical reactions (and hydration), and then to present later on reactions involving changes of valence (oxidation-reduction reactions).

The presentation of metathetical reactions begins with the study of acids, bases, and salts and their relations. Then follows a presentation of the phenomenon of electrical conductivity of solutions, the main facts concerning their ionization, their solubilities and how these together determine the taking place of metathetical reactions. The latter is demonstrated by means of conductivity trials made on solutions before and after they are mixed.

The student's knowledge of specific facts is then increased by presenting special metathetical reactions: the liberation, by metathetical reaction, of carbon dioxide, of sulphur dioxide, of ammonia and of hydrogen chloride. The properties and the most important reactions of these substances are shown in this connection,—also those of their chief constituent elements: carbon, sulphur, nitrogen, and chlorine (bromine, iodine, and fluorine, briefly in connection). Care is taken not to present here any oxidation-reduction reactions that might be omitted, and those that are presented (for instance, the formation of chlorine from hydrochloric acid, the oxidation of sulphurous acid to sulphuric acid)—these are not discussed in detail nor are their equations given. This is done to confine the student's attention to the metathetical reaction (and to the simple, accompanying reactions of hydration).

Since the reactions of the compounds of the metals involve nothing but metathetical reactions, these reactions are taken up next in order after the general discussion of the metathetical reaction.

How much of the reactions of the compounds of the metals should be taught in such a course as this? This has been, and possibly is still a great question. On one point, however, there is unanimity of opinion, and that is: *systematic qualitative analysis must not be attempted in a high school course.*

But this leaves us with the question: which of the reactions of the metals should be taught and how should they be taught? An examination of the laboratory manuals now on the market reveals great differences of opinion. Some manuals, such as Alexander Smith's and B. W. Peet's, present the reactions found in the ordinary outline for qualitative analysis, the only difference between this arrangement and that used in qualitative analysis being that in this case the reactions are presented disconnectedly, and outlines for the systematic analytical procedure are deliberately omitted.

Other manuals such as the *Laboratory Exercises* by Brownlee

and Others make no particular attempt to teach the reactions of the metals; but the latter book in Exercises 47 to 51 indicates that it is desirable to present certain features of this work. These features, which all authors are trying to present by their various methods, may be summed up as follows:

1. *To change* or transpose a metal *from one* of its compounds *to another* by means of the common reagents.
2. *To separate* a metal (in the form of a compound) out of mixtures of compounds of several metals.
3. *To recognize* or identify *a certain metal* in its compounds.

The first object is illustrative of the methods of manufacture of many commercially important salts and compounds from the commercial sources of the metal. The second is particularly illustrative of the chemical purifying of substances. The object of the third is self-evident. There can be no question as to the desirability of including some of this work in the course, and the only thing we need to consider is its extent and the method of treatment. With reference to its extent, that presented by *Brownlee and Others* is inadequate, while that presented by *Smith* and by *Peet* requires too much time. *Newell* uses the same method as *Smith* and as *Peet,* but he attempts to save time by lessening the number of exercises. This makes the work weak, if not utterly valueless. As a way out of these various difficulties, the following experimental procedure is suggested: take solutions of water soluble salts of the common metals and study their reactions with several general reagents. Then add special properties of some of the compounds of the metals such as the solubility of lead chloride in hot water, the hydrolysis of bismuth salts, the flame colorations, etc. Finally, add a list of exercises designed to make the student use these facts in the solution of special problems. The list of exercises given here is drawn up with this in view. These reactions of the metals give the student enough experience with the metathetical reaction to become well grounded in its fundamental facts.

The action of the most important inorganic reagents—the alkali hydroxides, the sulphides, etc.—are thus learned thoroughly by the student and he sees how the chemist proceeds to analyze substances. This exercise interests the student greatly and teaches all that qualitative analysis can teach without requiring the undue amount of time which the teaching of this special subject would require.

While the preceding exercise is being done in the laboratory, the time in the lecture room is devoted to the usual descriptive matter given in connection with about ten of the most common metals and their important compounds.

Some topics from applied chemistry are now introduced or

might have been introduced even earlier. The first subject suitable for this purpose is coal, its technical analysis and calorific power, etc. No special chemical knowledge is needed to discuss this topic and hence it may be studied at any time after the subject of oxygen has been studied. After the topic of metathetical reactions has been entered upon, then potable and irrigation waters may be taken up. Students should be shown how to judge their value and should be given an illustration of the methods of analysis of waters. An excellent example of technical chemistry which can be introduced here is the determination of the hardness of a water, the calculation of the amount and cost of reagents required to soften a thousand gallons, and the design of a simple plant for carrying out such work.

Then follows a brief study of some essential soil constituents not considered before: silica, silicates, silicic acid; phosphates and phosphoric acid. A brief presentation of the use of silicates is to be given here,—that is, in the manufacture of glass, earthenware, cement, and in the fluxing of ores in metallurgy.

Some of the effects due to the physical forces residing in the surfaces of contact between different kinds of substances are then to be studied because the phenomena they give rise to are of great technical importance and they are totally different from what the chemical nature of the substances would produce without the action of these surface forces. Surface effects produce the adsorption by soils of various salts from irrigation waters, the removal of coloring matter from solutions by charcoal and fuller's earth; they prevent the crystallization of sugar from syrup and they are the cause of the binding power of glue and of the puddling of clay.

The preceding topic naturally leads to a consideration of soils and fertilizers, which subjects should be presented at some length.

Electrolytic and battery cells are then to be studied at considerable length because electrochemical actions are very important technically and the study of these cells is purely a chemical study. Furthermore, a knowledge of the actions of these cells is the best foundation for the study of oxidation-reduction reactions that can be secured. Electrochemical actions are very complex and could not have been attempted earlier in the course unless the remarks made were confined to very simple statements such as that oxygen and hydrogen can be obtained by the electrolysis of water acidulated with sulphuric acid, etc. Such brief statements are all that could be given earlier in the course but they do not suffice to teach the subject as it should be taught.

The fundamental fact upon which the proper study of these electric cells is based is this: a cell is not a single unit but a collection of two independent units—the two poles, each with its surrounding liquid. This idea, without which no systematic pres-

entation of electrolytic cells or of battery cells can be made, is, unfortunately, not presented in most text-books, and although it has been thoroughly established for years and is recognized by all authorities, it has not been introduced in elementary text-books before this.

The study of the second great type of reactions—those which involve oxidation and reduction in solutions—must now be taken up. The terms *oxidation* and *reduction* are rather misleading; many changes to be considered under this heading do not involve oxygen in any apparent manner. As the terms are now used, their direct significance is as follows: oxidation is an increase of positive electric charges on an element or radical (or the abstraction of negative electric charges); and reduction is the reverse electric change. The conception involved here cannot be considered without a study of the action of battery cells, because the battery cell is, in a sense, *an experimental analysis* of oxidation and reduction reactions which presents the essential parts in their true relation. Any mixture in which oxidation and reduction take place represents merely the case in which the electric charges, instead of being transferred by means of conducting poles and their connecting wires, are transferred by direct contact between the two parts undergoing the changes in valence.

In this study of oxidizers and reducers the substances are taken up in the following order: 1. Elements (metals and halogens). 2. Simple compounds such as the iron salts, hydrogen sulphide. 3. Ternary oxygen compounds (nitric acid and its reduction products, concentrated sulphuric acid and its reduction products, oxy-halogen compounds). If time does not permit the study of all these topics, sulphuric acid and the oxy-halogen compounds may be omitted.

To conclude this study of inorganic chemistry, a brief study of the periodic system of the elements is to be given.

The fundamental principles of pure organic chemistry are then to be presented: the study should include the definition of, and relation between, the most important classes of carbon compounds (hydrocarbons, alcohols, aldehydes, acids, amines, esters, and ethers). Special mention should be made of commercially important members of each class.

The study of applied organic chemistry should then be extended to the commercial manufacture and important properties of animal and vegetable fats and oils, the carbohydrates, the three classes of foodstuffs, and the important fibers.

If time permits, three short experiments may be performed to demonstrate the law of Gay-Lussac (namely, the law that reacting gases show simple relations by volume). The three experiments given for this purpose in this book are particularly simple and

suitable. Avogadro's hypothesis and the determination of molecular weights may then be presented. However, this topic is not nearly as important a part of general chemistry as has been thought to be the case heretofore.

HOW TO TEACH ACCORDING TO SUCH A PLAN AT THE PRESENT TIME.

The order of the topics above is entirely different from the order now found in any descriptive text-book, and there is no text extant which includes all of these topics. Hence to teach according to such a plan, it seems to be necessary to secure a special new text-book. However, such a book need not displace the regular descriptive text-books now in use; in fact, it is better to secure a distinct book for the lessons and experiments apart from the descriptive text and then to use one of the text-books now in the market to draw from it the ordinary descriptive matter which many of them present very well. The use of two distinct books, one of which presents the series of lessons and exercises which introduce the subject, and the other of which presents the informational reading,—this has many advantages over the use of a single book for both purposes. The "lessons" require close study, while most of the descriptive matter merely requires "reading." If both descriptive matter and lessons are found in one book, it is difficult for the beginner to recognize which part should be learned in detail and which part should be merely read over. He may also fail to recognize the sequence of the unfolding of the subject and in a review he may find it difficult to gather up the most important parts.

For these reasons this book of lessons and exercises has been written. This book presents the order of study. It contains the directions for all the experiments to be performed together with the theoretical matter and the fundamental facts which must be learned and retained in order that the student may progress in his study of the subject.

As already stated, a descriptive text must be used in connection with this book of lessons and exercises. The latter takes the place of the laboratory manual, however, and in doing so it accomplished something that many consider to be essential to the successful teaching of chemistry, namely, that the order of the laboratory work determine the sequence of the topics studied. The class room discussions should *follow,* in a sense, the laboratory exercises. The subject should be presented in the laboratory, while the class room meetings should be used for drills, discussions, and quizzes.

SPECIAL DIFFICULTIES IN THE TEACHING OF APPLIED CHEMISTRY.

Many of the attempts made to introduce accurate information on practical subjects in the teaching of general chemistry have been worth very little, and some have even served to discredit both teacher and subject in the eyes of the general public. Adverse criticisms are due in general to one of two causes: the first is the ignorance of many teachers in the practical applications of chemistry, and the second is a mistaken method of presentation brought about by an undue zeal of some teachers to give this part of the subject prominence. These two causes will now be considered.

Unfortunately, many teachers of chemistry are not only comparatively ignorant of the details of the practical application of the subject, but their interest in the pure science inclines them to stress the pure scientific topics to the exclusion of the practical topics. The best way for teachers to overcome such difficulties is to *make a special effort to inform themselves on practical subjects.* They may not have obtained much, if any, of this information in college, and in any case such information along this line as they may have received while studying the subject will not be adequate for them to teach it properly; hence they must make a special effort, while teaching, to inform themselves by reading special books on practical topics, by noting the operations and practices in the trades around them, etc. Teachers in Texas schools should inform themselves particularly on the following subjects: soils, fertilizers, and irrigation waters, feed and foodstuffs; the technology of petroleum oils, tar oils, cotton seed oil, linseed oil; the manufacture of soap, paint, paper.

A teacher who has no knowledge of organic chemistry should study "Outlines of Organic Chemistry," by F. J. Moore, published by John Wiley & Sons. This book, though small, will give him the necessary scientific foundations for the teaching of applied organic chemistry.

The second cause of adverse criticism on the teaching of applied chemistry is the attempt made by some teachers to teach applied chemistry without any foundation of pure chemistry.

The writer has at hand some outlines prepared by prominent teachers of chemistry in various parts of the United States, in which an attempt is made to introduce practical subjects from the very beginning of the course. Long before the student has any knowledge of the simple chemical facts involved, these outlines present problems of water softening, the testing of coal gas for impurities, the solvent action of water on lead, the tests for organic matter in potable water, etc. Such information, though valuable in itself, becomes valueless when presented so early in the course that the student's lack of knowledge of pure chemical phenomena

prevents a recognition of the simple *fundamental* phenomena involved. The mere mechanical testing of certain constituents of a potable water before the student has even learned or seen reactions between pure salt solutions, such as the reaction between sodium carbonate and calcium chloride, cannot be of much value either as an informational or as a training exercise.

Another mistake is the selection of applications which are nothing but empiric operations. Thus we find various attempts made to present the chemistry of cooking, the chemistry of cleaning, etc., under which headings many useful topics are offered. When, however, such subjects are presented by themselves, and particularly when the presentation crowds out fundamental chemical phenomena, they degrade the course into the mere "trying out" of a number of shop recipes.

Of course the attempt has been made in this book to avoid such errors. The fundamental idea followed is to precede all portions of applied chemistry with an adequate treatment of the pure chemistry they involve. Furthermore, applied portions have been selected so as to present in the main the properties of the important commercial raw materials and their transformation into the chief manufacturing products so that the student may gain a true perspective of the value of materials in commerce, manufacture, and daily life.

Care has been taken not to select exercises or to present them in such a manner that the student gathers the notion that he is competent to examine and judge, as an expert chemist, various foodstuffs or other materials of commerce. It should be made clear to the student that the performing of the exercises is merely for the purpose of acquainting him definitely with the property of these materials; and the small amount of training he gets in handling these subjects fits him no more to do the work of a chemical analyst than a high school course in physiology fits a student to take the place of a physician.

Extensive work on the qualitative testing for poisons and adulterations of foodstuffs also is of questionable value. Since, as has just been pointed out, the object of the work is not the training of food analysts, and since the blind performance of many of the tests for poisons and adulterants gives the student no mental training nor any deeper insight into the nature and value of the main commercial materials, there is nothing gained from this work which might justify the expenditure of time and energy required for its performance.

BOOKS THAT MAY BE USED IN THIS WORK.

The first requisite in the way of descriptive text-books for the conductance of work according to this outline is still the regular text-book of which the following are good typical examples:

Brownlee and Others, *First Principles of Chemistry,* Allyn & Bacon; Hessler & Smith, *Essentials of Chemistry,* Benjamin Sanborn Co.; McPherson & Henderson, *Elementary Chemistry,* Ginn & Co.; Newell, *Descriptive Chemistry,* D. C. Heath & Co.

Books of this kind do not include as much of applied chemistry as is now required. For that reason it will be necessary to supply other books for collateral reading, and for this purpose the following are suggested. These books are all small and inexpensive and every school should secure from one to three copies per ten students of some of them so that they may be referred to frequently and extensively.

Industrial Chemistry, by B. K. Benson. Macmillan. Price, $2.00. Pp. 431. This is an excellent book which, in relatively few pages, presents a good account of the common engineering materials used in every-day life.

Nature and Use of Commercial Fertilizers, by G. S. Fraps. Bulletin of the Texas Agricultural Experiment Station. This is a bulletin of about 35 pages issued by the Experiment Station for free distribution. In it the nature and use of fertilizers is well presented.

Elementary Applied Chemistry, by Louis B. Allyn. Ginn & Co. Price, 60 cents. Pp. 127. In this booklet are presented quite a number of interesting exercises and chemical tests on various foods and household materials. This sort of work is undoubtedly very interesting and some of it may be assigned as optional exercises. As mentioned before, however, it is a mistake to think that the testing for adulterations or for poisons is a valuable exercise. The time is spent better in studying the useful raw materials and the production of the chief products from them.

Pure Foods, by J. C. Olsen. Ginn & Co. Price, 80 cents. Pp. 209. This is a very elementary, but interesting descriptive text on the composition and value of the common foodstuffs.

Chemistry and Its Relations to Daily Life, by Kahlenberg & Hart. Macmillan. Price, $1.25. Pp. 393. This book presents some elementary, practical information particularly on agricultural chemistry. The first portion of the book, which is devoted to general descriptive chemistry, is entirely inadequate for the *teaching* of the subject, but the latter half of the book may be read with profit by any student who has studied one of the ordinary introductory text-books.

The Chemistry of Plant and Animal Life, by Harry Snyder. Macmillan. Price, $1.40. Pp. 406.

Soils and Fertilizers, by Harry Snyder. Macmillan. [illegible], $1.25. Pp. 365. These two books by Harry Snyder are suitable for collateral reading. Though elementary in general character, yet they are decidedly more advanced than the two books immediately above them in this list.

Household Chemistry, by J. F. Snell. Macmillan. Pp. 307. $1.25. The latter half of this book presents, in a fairly extensive manner, the chemistry of foods, of digestion, and of the textile fibres. The book is intended for beginners in chemistry, but the first part of the book, when used as a text-book for beginners, is not likely to teach much except a few disconnected facts about chemistry. The latter part may be used by beginners, but it presents much more of foods, digestion and textile fibres than can be given together with other necessary topics in a course in general chemistry. However, the book should be on hand for collateral reading in every chemical laboratory.

SUGGESTIONS FOR CONDUCTING THE COURSE: WHICH FIRST, CHEMISTRY OR PHYSICS?

The question whether chemistry or physics shall precede in the high school course is a matter that should be left entirely to the high school people. Attention should be called to the fact that the progress of the class will naturally be slower if chemistry is given earlier in the course than if it is given during the last year. Furthermore, one topic must be given special consideration, that is the topic of battery cells and electrolysis. This subject should be given in the chemistry course rather than in the physics course because it is essentially a chemical subject. It cannot be presented without involving chemical considerations, and elementary chemistry cannot be presented properly without it.

TIME ALLOWANCE FOR THE COURSE.

The time given to chemistry in the high school should be no less than three recitation periods of forty-five minutes and two laboratory periods of at least double that time a week. Each double period for laboratory work should be uninterrupted, that is, there should be two consecutive periods. There should be no difficulty in arranging the schedule for this, because a study period may be placed just before or after the recitation period, and on days on which laboratory work is taken, the recitation period, together with the study period, then form the laboratory period. This arrangement is desirable for another reason: it frequently happens that the ratio between laboratory and recitation work temporarily should be changed in either way possible, because at times the recitation work requires more attention and at others the laboratory work.

Th.. rangement of the schedule here suggested permits of such a chai.ge, and hence is highly desirable.

TIME ALLOWANCE FOR PREPARATION OF LABORATORY AND LECTURE TABLE EXPERIMENTS.

Considerable time must be spent by the teacher in the preparation of special apparatus, in the preparations of solutions for the laboratory, and in the preparation of lecture table experiments. In addition to this there is the unavoidable labor of putting away the apparatus properly after use, and arranging the side shelf reagents, etc., after periods of laboratory work. As a rule superintendents and principals either do not realize how time consuming this work is or they are disposed to minimize its importance. Some will consider that this is essentially janitorial work, for which some cheap help might either be hired, or which if done by the teacher does not deserve any consideration as a part of his teaching work. This is utterly wrong. The teacher of chemistry should be allowed time enough to do such work properly, and such time should be a part of his teaching time, and not of hours after school work. If the suggestion made above for the scheduling of the laboratory and of the recitation work is followed, then in addition to the double period each day, kept open throughout the week for chemistry, there should be set aside another period each day for the teacher to look after the equipment. In this way he will have two periods three times a week and one period twice a week, a total of eight periods to prepare his experimental work. This is not excessive and will be very profitable to the school. If classes are large, the teacher must be given, in addition, assistants to aid him in cleaning up the laboratory, etc. Such service can be secured very reasonably from some member of the chemistry class. The cleaning up should not be done without the direction of the teacher, because he should know where everything is placed.

However, such time allowance, etc., puts a responsibility upon the teacher which he must not shirk. A chemistry teacher must be "up and about" doing experimental work with his own hands. All "sitting back" and letting the students only do experimental work or ordering around some assistant to prepare experiments and reagents is indicative of a person unfit to be a teacher of science. He must be the *chief experimenter;* he must be possessed of a desire to do experimental work, and with his own hands attend to matters in the laboratory.

It is questionable whether extensive lecture demonstrating has a value proportionate to the cost of the teacher's time required for it, because frequently students fail to grasp the details of experiments shown on the lecture table. In general, it may be said that any experiment performed by the student is worth much

more than the same experiment performed by the teacher on the lecture table. For that reason the experiments of this book have been selected and designed so that they *all* may be performed easily by students in the laboratory. Of course there is no objection to the teachers performing some of them on the lecture table in order to gain time in the laboratory.

MANNER OF CONDUCTING LABORATORY WORK.

Beginners in chemistry are frequently inclined to do their laboratory work in a mechanical manner merely, and the newness of the subject inclines them also to take too much time in the performance of experiments. Hence the teacher must use a method of conducting laboratory work which will keep the mental aspect of the subject constantly before them and force them to do their work expeditiously. This may be done by conducting the laboratory work in a manner similar to that of conducting class work. Thus at suitable times during the periods of laboratory work, the teacher should discuss with the whole class the chemical changes dealt with, and drill his pupils on all related matter. He should strive by all means possible to enliven the activity of laboratory practice, realizing that it is in the laboratory rather than in the lecture room that chemistry may be taught and learned.

In the treatment of the experimental material the aim should be to teach the common properties of substances in the *broadest manner*. Thus in connection with the preparation of oxygen, the student should not be taught that "*the laboratory method* for the preparation of oxygen consists of heating a mixture of potassium chlorate and manganese dioxide," but he should be taught that "there are some compounds of oxygen that decompose when exposed to a sufficiently high temperature and yield oxygen as one of the products of decomposition. Of course not all substances break up in the temperatures at our command, yet quite a number do so, among which may be mentioned lead peroxide, mercuric oxide, potassium chlorate, potassium nitrate, etc. These should be remembered as substances not only rich in oxygen but that yield it up when exposed to a moderately high temperature obtainable in the laboratory." By this means the student has not only learned how oxygen may be prepared, but he has learned to some extent the behavior of oxygen compounds exposed to different temperatures. The information thus conveyed is farther reaching and more general than the mere *preparation of oxygen*. This effort to teach something of *general* bearing in connection with the specific information conveyed should be made wherever it is possible. In this Course of Lessons and Exercises in General Chemistry this principle is applied rather carefully, as may be noticed by looking at the first few topics given.

In the teaching of experimental work it should be emphasized that an experiment is valuable *only if it is clearly remembered* by the student. There exists a mistaken notion that experimental work is intended primarily to train the student in the performance of such work somewhat for the same reason that training is necessary in carpenter work, metal work, etc. Such training is only an *incidental* object which is attained without particular effort if the work is done properly. The *main* object is to learn something about the substances, and the whole value of the work is lost if the experiment is forgotten. It is practically true that the value of the course is proportional to the accuracy with which everything, including details of a set of well selected experiments *is remembered.*

NOTE ON QUANTITATIVE EXPERIMENTS.

Although quantitative experiments are usually introduced early in the course, yet it appears to the writer that it is inadvisable to do so. It is only when the student has a fairly extensive knowledge of chemical *phenomena* that he can appreciate *quantitative* relations. However, later in the course quantitative experiments are extremely valuable.

A number of quantitative experiments are given in this book, but contrary to the common practice of giving exercises in pure chemistry only, quantitative experiments in applied chemistry have been given here,—for example, illustrations of the examination of waters, coal, soap, linseed oil, etc. It has been found that such determinations reveal to the student the means of judging the value of materials, and hence they heighten his interest in the subject.

THE NOTE-BOOK.

The first thing to insist upon in the note-books is correct spelling and correct composition.

Next, all attempts to use blanks, to be filled in, or detailed "patterns," to be followed for the writing up of experiments, are to be discouraged. A few general directions are naturally necessary, but any approach to a "formula" to be used in writing up experiments should be decidedly discouraged.

The first general direction given to students for writing up their notes is to call attention to the fact that the name of the book should be indicative of its use; it should be a *note-book,* and *not* a re-written text-book or a book of essays. If in performing the experiments, printed directions have been followed, then these *directions should not be copied into the note-book.* Of course such directions should be definitely referred to in some such manner as this: "Experiment (number) ———, page ———, in

Laboratory Manual was performed in full (or "with the following exceptions"). If *additional* experiments in which printed directions were not followed have been performed by the student, then these may be written out in full.

In the note-book the experiments may be numbered merely for the sake of indicating the order. However, the most important thing is to *devise for each experiment a heading* which states clearly the nature and object of the experiment. Considerable time may be spent in thought in order to devise headings that may be properly significant. A suitable heading is just as important in itself as all the notes that follow, and the devising of proper headings is one of the best means to force the student to realize what he is doing and what he is doing it for. The heading should not be merely a general term, and not more than one definite subject should be put under it. Thus it is absurd to give the heading "oxygen" to all the experiments given in connection with the study of that subject. Some of the experiments in connection with oxygen have been made with the view of demonstrating with what chemicals and with what operations it may be prepared. Other experiments may have been made with the view of preparing certain bottles full of the gas and showing some of its common properties. Hence it would be logical to head one experiment as follows: "To demonstrate with what substances and what operation oxygen may be prepared." The other experiment should be headed somewhat as follows: "The preparation and collection of oxygen gas and the demonstration of some of its properties."

The assignment of separate headings to distinct parts of experimental work should not be carried to the extreme. It is unnecessary to divide the last experiment discussed above into the following: *first,* the preparation and collection of the gas; *second,* the combustion of sulphur in oxygen, etc. The collection of several operations under one heading naturally requires thought, and during the first part of the course the student will have much difficulty with it, but the benefit gained, both as far as grasping the subject is concerned and as far as training in composition is concerned, will amply repay the time spent upon this work.

In the body of the "write up" the first thing to be given is a direct reference to the directions followed, e. g.: *"Smith,* Exp. ———, page ———, was performed *in full"* (or "with the following exceptions"), etc.

Then should follow a brief definite statement of what was actually noted or observed, which has not been given in the printed directions referred to above. For example, under the last heading mentioned would appear: sulphur, carbon, phosphorus and sodium after they were heated to their kindling temperatures burned vigorously in the oxygen gas. The product of combustion of carbon

(carbon dioxide) is an invisible, inodorous gas; that of sulphur is an invisible gas with suffocating odor; that of phosphorus is a white solid and that of sodium is a white solid. Treated with water, these substances give solutions the first three of which turned blue litmus red and the last turned red litmus blue. The equations for the chemical actions which take place during combustion and afterwards on treatment of water are as follows: ". . ."

The notes should always show the equations of the reactions in the experiment. Care must be taken by the teacher to see that they are written correctly.

The frequent drawing of figures—particularly of such things as test tubes, burners, etc., is a waste of time. A figure should be drawn only if the apparatus is so elaborate that the figure is essential to accuracy and brevity of description; and when a figure is drawn it should be drawn carefully,—in *projection* or *plan* rather than in perspective. It is advisable to use celluloid patterns as aids in drawing figures. They may be obtained from the Central Scientific Company of Chicago.

IS THE USUAL NOTE-BOOK DESIRABLE?

It is easily seen from the foregoing that the type of note-book which is an elaborate copy of the laboratory manual is not desirable. It is objected to because the writing of the notes is liable to be done in a thoughtless, mechanical manner, it consumes an undue amount of time, and tends to develop the idea that the work may be forgotten as soon as the notes are written up.

Just the opposite result should be obtained:—much thought should be spent on how and what to record; what is put down should be a note which amplifies the printed directions but does not copy them; only small amounts of time should be required for the *writing* of the notes; and any experiment that is worth doing is worth being remembered—at least as long as the course lasts. For these reasons the style of note-book which is in rather common use is not desirable.

Possibly the only good reason for asking students, in writing up their note-books, to describe at length the experiments performed is the fact that the writing of a detailed description will tend to make them more accurate in the observation of the experimental details, and that it trains them in describing carefully what they have done. It must be admitted that these objects must be attained in some way, but there is another way of attaining them and that is by asking students frequently in class quizzes to write out from memory the details of a recently performed experiment. Ample time should be given in these quizzes to allow the student to compose his answers carefully and in grading the

answers the composition of the answers should be considered. This plan produces better results with less labor on the part of the teacher than the elaborate writing up of note-books.

SUGGESTIONS ON CHAPTER I: THE PREPARATION AND PROPERTIES OF OXYGEN AND THE FUNDAMENTAL FACTS OF CHEMICAL CHANGES.

These lessons are essentially "laboratory" lessons: the class room discussions should *follow* the laboratory exercises.

Begin the laboratory work "class fashion." Thus, tell the students to take out their Bunsen burners, and direct them orally how to take these apart, put them together again, etc., so that all students may perform each part simultaneously and expeditiously.

In the first chapter note carefully the manner in which symbols are introduced,—that no mention is made of atoms and molecules,—that an elevated temperature and not the addition of heat is spoken of in connection with the decomposition of potassium chlorate. Tell the students to commit to memory the names of the chemicals used in the experiments and also the equations given. Drill them vigorously on this memorized information. Make up problems based on the equations given.

Read, in this manual, the section on writing up notes, and give the students the general directions for the entry of observations in a note-book.

In order to economize time, the teacher should show the burning of iron in oxygen: use a bundle of fine iron picture cord; attach it to a deflagrating spoon, warm the picture cord and dip it into powdered sulphur, then lower it into a large bottle full of oxygen upon the bottom of which has been placed a layer of sand to protect the glass from the drippings of melted iron oxide.

Collateral reading should be assigned, in a text-book, on *oxygen* as well as on *the atmosphere.*

Corrections of gas volumes *for pressure* and *for temperature* may also be given if the time permits; but this topic is not nearly as important at this time as some books indicate.

SUGGESTIONS ON CHAPTER II: THE PREPARATION AND PROPERTIES OF HYDROGEN AND AN ILLUSTRATION OF THE SECOND FUNDAMENTAL FACT OF CHEMICAL REACTIONS.

Insist that the students learn (a) the equations given in this lesson, (b) the order of the metals in the list given, and (c) the general facts covering the interaction of all metals with all acids. Drill on the equations by means of numerical problems based on them. But little text-book reading can be assigned in connection

with hydrogen,—in general, only the paragraphs on the physical and chemical properties. If gaseous diffusion is demonstrated before the class, then this topic may be touched on—otherwise it should be omitted: it is not essential to the subject.

SUGGESTIONS ON CHAPTER III: A REVERSIBLE REACTION AND AN ILLUSTRATION OF THE CHANGE OF THE REACTING TENDENCY OF SUBSTANCES DUE TO CHANGES IN THEIR CONCENTRATIONS.

The first part of the lesson is self-explanatory.

The experiment of showing the reaction between steam and metals may be performed by the teacher—thus saving the student's time.

It is strongly advised that other facts and topics be not introduced in connection with this lesson:—many books introduce here the volumetric composition of water, electrolysis, and elaborate considerations of the combining ratios between different elements: all of these may be omitted for the following reasons: volumetric relations between reacting gases are to be left till much later in the course, or they may be omitted altogether; electrolysis requires special and more extended treatment to be given later; and the effort to show beginners the *origin* of atomic weights is likely to be unprofitable.

A *part* of the descriptive matter given in text-books in the chapter on water and on hydrogen-peroxide may be assigned, but is not essential.

SUGGESTIONS ON CHAPTER IV: THE LAWS OF RELATIVE COMBINING WEIGHTS AND THE THEORY DEVISED TO RENDER THEM PLAUSIBLE.

Do not treat this subject too extensively: insist merely on their knowing the laws which require the atomic theory for their explanation, and insist that the students see how these facts (and *only* these facts) are explained by the theory. Avoid any reference to the so-called molecular theory, and do not attempt to show how the atomic weight table was devised: it will be found unprofitable to attempt these subjects at this part of the course.

In the assigning of collateral reading be careful to select only those parts in text-books which deal with this and not with a further extension of the theory.

SUGGESTIONS ON CHAPTER V: ACIDS, BASES, AND SALTS.

Acids, bases, and salts are studied next because they form the three most important chemical classes of inorganic substances,

and the reactions between acids and bases are the most important and most striking of the simple reactions between ions. They are, in a sense, the best examples with which to begin the great subject of "metathetical reactions in solutions."

To clean the burettes which the students are to use, they should be kept for several hours in a mixture made of concentrated sulphuric acid and chromic acid: this is easily accomplished by placing them with the upper ends into a vessel filled with this mixture, and filling the tubes by suction. To gain time, the teacher should clean these burettes before the laboratory period.

The burettes should be returned to the storeroom after this exercise: they should be put away *clean,* and with the glass cocks removed and tied on with a string:—or with the pinch clamps removed.

If it is desired to gain time, the preparation of magnesium chloride and of lead nitrate may be omitted; also, the experiment on the effect of solubility upon the interaction of acids and bases may be omitted.

The objects of the experiments given should be clearly recognized by the students, and all the facts, as well as the experiments, should be clearly *remembered.* Thorough and frequently repeated drills are necessary to gain this end.

In most texts the arrangement of the subject matter of this lesson is so different from the arrangement here given that no definite portions of the texts can profitably be assigned in this connection. Extensive reading is really unnecessary—if not actually harmful—in this connection. What is needed is close attention to—and retention of—a few facts and statements such as those here given.

SUGGESTIONS ON CHAPTER VI: IONIZATION AND THE GENERAL RELATION BETWEEN DISSOLVED ACIDS, BASES, AND SALTS WHICH RESULTS IN METATHETICAL REACTION.

The conductivity experiments given in this chapter are exceedingly instructive and they are easily performed. No special conductivity vessels and no platinum poles are required: the copper wire ends are merely to be held in beakers. Care must be taken in only one respect,—namely, to hold the wires the same distance apart and to insert them to the same depth in all the liquids of each comparative trial.

Ammonium hydroxide and ammonium salts are used in some of the experiments:—it will be advisable for the instructor to mention that the ammonium ion has the composition expressed by the symbol NH_4 and that it is similar in property to the sodium ion, but further explanatory statements are unnecessary.

With the exception of *Brownlee,* Arts. 96-107, there is nothing in the elementary text-books that will aid in the study of this chapter. It is probably unnecessary to add anything to the presentation given here and it may be even advisable to *confine* the student to a close study of what is here presented. The entire contents of this chapter requires frequent repetition and drill because the experiments are all of general import, and the general facts are employed constantly in the further study of the subject.

SUGGESTIONS ON CHAPTER VII: CARBON, SULPHUR, NITROGEN, THE HALOGENS, AND RELATED COMPOUNDS.

The topics studied in this chapter are primarily of informational value and their study is to be carried on in the simplest manner possible. The corresponding parts in text-books should be read by the students in connection with this work. Although other experiments may be added, if desired, yet much time should not be spent on this work, and the addition of other experiments is inadvisable.

Suggestions on Carbon.—Present some of the properties of the element, the discussion of the flame, some descriptive matter concerning the importance of carbon monoxide on account of its presence in water gas and its use in the reduction of ores (e. g., of iron ores). In connection with the reactions of carbon dioxide emphasize that the portion dissolved in water is largely hydrated; whenever it acts, in solution, as an acid on a base, then it is H_2CO_3 which is the acting substance, and not CO_2. A separate equation should always be written to express the hydration and dehydration that may precede or follow a metathetical reaction. Thus when carbon dioxide is absorbed by lime water the following reactions take place in the order here given:

(a) $CO_2+H_2O=H_2CO_3$
(b) $H_2CO_3+Ca(OH)_2=CaCO_3+2H_2O.$

These reactions should *not* be combined into the following expressions:

$$CO_2+Ca(OH)_2=CaCO_2+H_2O. \quad \text{(Avoid this!)}$$

Suggestions on Sulphur.—Deal briefly with the properties of the element (the phenomena presented by melted and cooled sulphur, etc., need not be considered). Emphasize the source and extraction of commercial sulphur.

Deal with hydrogen sulphide very briefly here. Make some iron sulphide and liberate hydrogen sulphide from it. Note that the gas is poisonous. The reactions involved in these examples are mainly simple or metathetical, and the complex oxidation reactions

of hydrogen sulphide must be omitted here. The use of hydrogen sulphide as a laboratory reagent will be sufficiently illustrated later.

Note that sulphur dioxide is to be prepared by means of the reaction between sulphites and acids, and not from concentrated sulphuric acid and copper. The method here recommended is more convenient and fits here better pedagogically because it involves a metathetical reaction while the reaction between concentrated sulphuric acid and copper is an oxidation-reduction reaction.

In writing the equations with sulphur dioxide, its hydration and dehydration should be expressed by an equation separate from any metathetical reactions—as was advised for carbon dioxide.

The main chemical property of sulphur dioxide or sulphurous acid is its tendency to be oxidized to sulphuric acid.

The commercial production of sulphuric acid by the contact method may be given here. If the old English method is given, no reference need be made to the formation of nitrosyl sulphuric acid. It is perfectly correct to state that *NO* takes up oxygen to form NO_2 and this change takes place more readily and hence faster than the *direct* reaction between SO_2 and the oxygen of the air. The oxides of nitrogen are merely *catalytic agents,* and the impelling tendency of the action is always the tendency of SO_2 to take up oxygen.

Suggestions on Ammonia.—Point out the commercial source of ammonia, its use in agriculture, and its high price. Also stress the fact that ammonia hydrates in solution.

Suggestions on Hydrogen Chloride.—In order that a chloride and an acid may react metathetically, it is necessary that water be absent so that very little hydrogen chloride can be dissolved in the mixture. Since in the absence of water the mixture actually reacts, while no reaction takes place in the presence of water, it may be inferred that the concentration of hydrogen chloride in the mixture is too small to prevent the extensive combining of the hydrogen and chlorine ions. This is probably the relation in the mixture which brings about this metathetical reaction.

Suggestions on Chlorine.—The reactions involved in the preparation of chlorine are all complex reactions of oxidation and reduction, hence the preparation of chlorine does not fit into our general plan at this point. However, it is desirable to demonstrate here the properties of the element. For the reason just given, the details of the reactions involved in the preparation of chlorine *are not considered* and the general fact alone is given, namely, that it is prepared by the action of oxidizing agents upon hydrochloric acid. The oxidizing agents serve in a sense as suppliers of oxygen merely, and the oxygen that they supply combines with the hydrogen of the hydrochloric acid to form water. The fol-

lowing equation represents this change and is the only one that should be given and learned in this connection:

$$O+2HCl=H_2O+2Cl.$$

Use several oxidizing agents to illustrate this general method of producing chlorine.

In preparing hydrobromic acid and hydriodic acid, concentrated phosphoric acid is employed because this does not oxidize HBr and HI while concentrated sulphuric acid oxidizes them.

SUGGESTIONS ON CHAPTER VIII: THE ACTION AND USE OF GENERAL REAGENTS.

The following exercise on separating and identifying metal ions is not merely an introduction to qualitative analysis:—it is an exercise designed to teach, more effectively and with a lesser expenditure of time, all that may be gained by teaching qualitative analysis. Teachers should bear this in mind. This exercise should be neither slighted nor should it be overdone as though to expand it into a *course* of qualitative analysis. The mere determination of "unknowns" is not the object of this work: the object is, rather, to show how facts may be used to identify substances or to separate them from a mixture,—the chemist's most fundamental problem.

The unknowns to be given to students may contain from one to three metal ions even from the very outset, but care must be taken to put only such metal ions into a mixture which can be definitely recognized in each other's presence or which can be easily or definitely separated from each other. Before handing out a mixture, the teacher should figure out exactly how he could work it out with the facts furnished in this chapter. *Avoid these combinations*:—Cu and Cd, Al and Zn, Pb and Bi, mercuric ion and Bi, mercuric ion and Pb, Mn with Al or Fe or Ni or Zn. Never put more than three metal ions into a mixture, but do not let the students know of this limit. Do not take too much time for "unknowns":—five mixtures will probably be as many as a student should work out,—even three is enough. There is other, more profitable, work to be done.

While the laboratory periods are taken up with the work of this chapter, the class room time should be spent on the usual descriptive matter given in text-books under the alkali metals and under the alkaline earth metals. A special effort should be made to point out the "source" salts of these metals and the production of the commercially important compounds from the source salts. It is important for students to learn that the main source salts of sodium and potassium are their chlorides and that the economic

production of their other compounds can be accomplished only in two important ways: (1) conversion to carbonate, by the Le Blanc or the Solvay process; (2) conversion to hydroxide in some special electrolytic cell of extremely thoughtful design (Castner Cell, Townsend Cell, etc.). All other salts of sodium and potassium in general are made from the carbonates or hydroxides.

SUGGESTIONS ON CHAPTER IX: FUEL AND INDUSTRIAL WATERS.

The most reliable and extensive information concerning the fuels of Texas is found in the following publication, which is distributed free by the University of Texas: "The Fuels Used in Texas," by William B. Phillips and S. H. Worrell, Bulletin No. 307 of the University of Texas, Bureau of Economic Geology and Technology.

An excellent treatment, from the practical standpoint, on combustion and fuels, is found in Benson, *Industrial Chemistry,* chapters 4 and 5.

The Graefe gas calorimeter used in this chapter can be secured in the market (Eimer and Amend Cat. No. C2648D,—$25). It can be made at home at a very small cost. A local tinner will make the calorimeter proper for about three dollars. This vessel has the following dimensions:

Diameter of vessel, 3 5-16 inches.
Length of vessel, 13 inches.
Diameter of lower part of inner tube, 1¾ inches.
Length of lower part of inner tube, 9 inches.
Diameter of upper part of inner tube, 11-16 inch.
Length of upper part of inner tube, 5¾ inches.

The vessel should be made of sheet copper or sheet brass. The five copper gauze discs which are to be put into the lower part of the inner tube are strung on a stout copper wire knotted suitably to hold the discs apart. Probably it is advisable *to buy one* of these calorimeter vessels and then to have others made with this as a pattern.

The large glass bottle which serves both as the gas holder and gas meter, may be constructed from any tall, one-gallon glass bottle. It should be provided with a well fitting rubber stopper with two holes, through which extend two rather wide glass conducting tubes, one reaching to the bottom of the bottle and the other terminating just below the stopper. Above the stopper both tubes are bent at right angles. To fill water into the bottle, a glass funnel is attached, with a short piece of rubber tube, to the glass tube which extends to the bottom of the bottle. This funnel is suspended from a ring stand as shown in the figure given in

the text, and a vessel is placed beneath the funnel to catch the water which overflows while operating the calorimeter.

For the work on industrial waters there must be prepared a 1-50 normal solution of sulphuric acid and also one of sodium carbonate. For this purpose secure from a chemical dealer or from some chemical laboratory nearby two liters of normal sulphuric acid. Measure out with a burette 20 c.c. of this acid, putting it into a volumetric liter flask. Fill this flask to the liter mark with distilled water and shake the contents well to mix them.

To prepare the 1-50 normal sodium carbonate solution, weigh out roughly 2.5 grams of pure dry sodium carbonate. Put it into a two-liter flask and add (approximately) two liters of water and shake the contents well to mix them. Titrate this solution against the 1-50 normal sulphuric acid solution prepared above (with methyl orange as an indicator), and then make this solution exactly 1-50 normal, as follows: calculate how many c.c. of this solution should be diluted with water so as to make one liter of 1-50 normal solution, pour the solution into a one-liter volumetric flask and remove by means of a burette as many c.c. as should be replaced with water. Then re-fill the empty space up to the mark with water. The quantity of solution on hand will suffice to prepare *two* liters of exactly 1-50 normal sodium carbonate.

For the optional exercise on the determination of chlorides or sulphates in an industrial water there should be on hand for every ten students—

One water suction filter pump (Eimer and Amend Cat. C, No. 5624,—$2.00), one filter flask with heavy rubber connecting tube. This flask can be assembled by using a 500 c.c. ordinary wide-mouth bottle, a two-hole rubber stopper, a 3-inch glass funnel, and a bent piece of glass tubing,—all as shown in the figure given in the text. A piece of wide, thin rubber tubing like the inner tube of a bicycle tire, 1½ inches in length, is stretched around the upper edge of the funnel so that the conical filter may fit air tight around the upper edge of the funnel.

All supplies necessary for these experiments have been listed either in Part I of this Bulletin, or in the supplementary list given at the end of this Teacher's Manual.

Of the alundum filters there should be secured at least one for every student. Order of the Norton Company, Worcester, Mass., alundum conical filters, No. 7056, suitable for silver chloride and barium sulphate (price 40 cents apiece). These can be used again many times, particularly if only one kind of a precipitate is put into them.

The solutions to be given to the students for the determination of chlorides and sulphates may be samples of local waters, or better, they may be prepared as follows: dissolve 3 grams of sodium

chloride or 7 grams of magnesium sulphate in a liter of water: 100 c.c. of these solutions will give a suitable amount of precipitate.

If for the determination of hardness in waters no suitable samples of natural waters may be obtained, then artificial samples may be prepared as follows: for temporary hardness convert a solution of clear lime water into a solution of calcium bicarbonate by saturating it with carbon dioxide; for temporary hardness saturate some distilled water with calcium sulphate.

SUGGESTIONS ON CHAPTER X: SOME EXPERIMENTS ON SILICATES AND PHOSPHATES TO ILLUSTRATE THEIR INDUSTRIALLY IMPORTANT PROPERTIES.

In connection with silica, a *brief* text-book study should be made of the materials used in the manufacture of glass, hydraulic cement, and earthenware. This consideration should not be extensive. The setting of cement and the action of soils and fertilizers should not be taken up until after the next chapter has been studied.

In connection with phosphates, the preparation of phosphorus—by reduction of phosphates with carbon—and the manufacture of matches should be mentioned. Attention should be called to the fact that phosphoric acid is made directly from phosphates and not from phosphorus: this is the reverse of the procedure followed with sulphuric acid for the self-evident reason that the source material in one case is phosphates and in the other free sulphur.

SUGGESTIONS ON CHAPTER XI: THE EFFECT OF SURFACE SOURCES.

Direct the students to secure copies of the bulletin of the Texas Experiment Station entitled "On the Nature and Use of Fertilizers," by G. S. Fraps. Several lessons should be spent on this bulletin. In this connection the following fact should be pointed out to the students: chemical analyses of soils are of practically no value in determining the need of a soil for fertilizers. Never advise anyone to have soils analyzed for this purpose. The need of a soil for fertilizers is determined by direct experiments with plants.

It is advisable to urge the students to do as much collateral reading on soils and fertilizers and on the chemistry of plant and animal life as possible. The books suggested in the introduction are quite suitable for this purpose.

SUGGESTIONS ON CHAPTER XII: ELECTROLYSIS AND THE CHEMICAL CHANGES AT THE POLES OF ELECTROLYTIC CELLS.

The usual experiments on electrolysis present an *apparently* simpler apparatus than that used here; but the simplicity is not really there, and hence the appearance is misleading. An electrolytic cell is not a unit; *three* distinct and qualitatively independent actions take place in it, and in order that the actions in any electrolytic cell may be understood, the *three* actions must be shown separately:—that is the object of the experimental work presented in this lesson.

The main reason for selecting this method of presentation is to obtain a logical introduction to the action of battery cells and "oxidation and reduction" reactions. In fact, electrolysis itself is not completely presented in this lesson because the action of battery cells must be known before all the facts of electrolysis can be understood.

Many teachers may question the use of the electron theory in explaining the actions in electrolytic and battery cells. The reasons for adopting it are the following: at present it is better supported by experimental facts than any other theory; it simplifies the explanations of all electro-chemical phenomena; as regards conduction through metals, it is fully as simple—if not simpler—than the old "non-materialistic" theory of electricity.

With reference to the last point,—the conduction of electricity through metal—it should be pointed out that the flow of electrons through a wire is in exactly the opposite direction to the flow of *the current* as it is ordinarily spoken of.

Several important commercial applications of electrolysis should be brought to the student's attention in connection with this subject. A few of these subjects are indicated below.

The electrolysis of sodium chloride solutions for the production of sodium hydroxide and chlorine: this operation is complicated by the great solubility of chlorine, and by the great mobility of the OH' ions. A diaphragm can be used to keep the chlorine from getting to the cathode, but it cannot hinder the OH ions from being "transported" toward the anode in great amount because the electric transport moves the OH ions much more than any other anions present. On account of this difficulty, the electrolysis of sodium chloride solutions cannot be done economically except by means of very remarkable contrivances. This should be pointed out to the students and then they should be told to read about the Castner double cell.

Since successful diaphragm processes have been devised, it is quite profitable to present the details of one of the best of these—the Townsend cell.

Mention should be made of the metals which are used for electroplating—copper, silver, gold, nickel and brass—and the general plan of operation as given in the text-books should be pointed out. There are so many special points to be considered in practical electroplating that it is useless to attempt to teach the *details* of this operation here. The student should be told that there are many details to be observed in "plating." Mention should also be made of the metals *refined* by electrolysis:—copper, silver, gold, nickel, and lead. The underlying principles will be taken up later in the study of battery cells. Nothing can be done here beyond mentioning the general plan of the operation of metal refining. But it should be impressed upon the student that refining is accomplished only when certain conditions are maintained. These conditions will be indicated later.

The extraction of aluminium, and of sodium, by the electrolysis of molten salts should be read up in text-books. The reasons why these metals cannot be deposited from aqueous solutions should be apparent to the students from the result with cup 7 in the experiment. Attention should also be called to the fact that the difficulty in the extraction of aluminium lies not only in the electrolysis, but also in the fact that pure aluminium cannot be obtained except with very pure materials because the conditions which bring about the reduction of aluminium also bring about the reduction of most other common metals.

SUGGESTIONS ON CHAPTER XIII: BATTERY CELLS AND OXIDATION-REDUCTION REACTIONS.

Battery cells are presented here at length for several reasons. In the first place, elementary electrochemical phenomena depend more largely on chemical facts than on physical facts, and hence they can be studied better in connection with a general study of chemistry than with the study of physics. In the second place, electro-chemical cells exhibit in their proper relation all parts which enter into an oxidation and reduction reaction. The equality between the amounts of oxidation and reduction in a reaction,—which relation otherwise is hazy to the student, or appears to rest merely upon definitions or the instructor's say so,—this equality is not only plainly shown by the action of the battery cell, but the changes in valence become a reality to the student because the necessary accompanying flow of current in battery cells is a reality.

The contents of this chapter must be taken up exactly in the order given, and the student's attention should be confined to this subject during both lecture and laboratory hours. Vigorous drill is necessary to fasten this subject in the student's mind.

If time is to be saved, then the portion of this subject coming after the section on nitric acid may be omitted.

As a conclusion to the action of battery cells the teacher may present the construction and action of several commercial battery cells, particularly of the lead-storage cell and the so-called dry cell. A few words concerning the pole reactions in these cells may be of service here.

In the lead storage cell, the negative pole consists of lead and lead sulphate immersed in dilute sulphuric acid. The pole reaction here is

$$Pb^{\circ} + SO_4'' \rightleftarrows Pb\ SO_4 + 2(-)$$

When the cell furnishes current as a battery, the negative current goes out of the cell at this pole and the reaction must take place so as to produce electrons: hence the reaction takes place in the sense of the upper arrow; but when the cell is charged, then the electrons are sent into the cell at this pole, and the reaction takes place according to the lower arrow. It should be remarked that on account of the slight solubility of lead sulphate, the liquid contains very little of it, and most of it separates on the electrode as soon as formed; vice versa when the cell is recharged.

The positive pole of the storage cell consists of lead dioxide and lead sulphate (also immersed in dilute sulphuric acid). The pole reaction is—

$$PbO_2 + 4H^* + SO_4'' + 2(-) \rightleftarrows PbSO_4 + 2H_2O$$

When the cell acts as a battery cell, this (positive!) pole receives electrons—hence the reaction takes place according to the upper arrow, and when the cell is charged, the reaction takes place according to the lower arrow.

The "so-called" dry cell contains a negative pole of zinc in contact with a saturated solution of ammonium chloride. The pole reaction consists of the change of zinc metal to zinc ion—

$$Zn^{\circ} \rightarrow Zn^{**} + 2(-)$$

The zinc ions immediately react with NH_4 ions—

$$Zn^{**} + 2NH_4^* \rightarrow (NH_3)_2 Zn^{**} + 2H^*$$

and the H^* ions react with the next NH_4^*, etc., all along the line to the other pole.

The other (positive) pole consists of an *inert* carbon pole packed in manganese dioxide soaked with a saturated ammonium chloride solution. The reaction at this pole is—

$$2H^* + O^{\circ}\ (\text{from Mn } O_2) + 2(-) \rightarrow H_2O$$

The origin of the H^* ions was pointed out above. The $Mn\ O_2$ becomes $Mn_3\ O_4$.

The electrolytic refining of metals may be explained after the section on the "Back Electromotive Force of Electrolytic Cells" has been studied. The essential points in the electrolytic refining of copper, for instance, is this: copper and all those metals which have a *greater* tendency than copper to form compounds—namely, lead, iron, zinc, etc.—enter the solution from the impure anode,—that is, they form *compounds;* but, under proper conditions, only copper is deposited at the cathode because lead, iron, zinc, etc., require a more cathodic potential than copper for their deposition, and such a higher potential is not exerted at the cathode as long as there is enough copper present at the cathode to carry the current from solution to cathode. It follows that these compounds of zinc, iron, etc., accumulate in the solution and hence the solution must be changed occasionally.

If the anodes contain metals like silver, gold, etc., which have a *lesser* tendency than copper, to form compounds, these metals are not changed to compounds but drop off when the surrounding copper is acted upon; they accumulate in the "sludge" at the bottom of the bath. Hence copper is the only metal which reaches the cathode and for which there is enough electromotive force to deposit it.

In connection with this subject the students should read the ordinary descriptive matter given in the text-books under the headings of the metals gold, silver, copper, lead, iron, zinc and tin. Attention should be paid to their metallurgical extraction, the properties of the metals and their uses, special useful compounds such as white lead, zinc white, lead chromate, chrome green, etc., as pigments for paints: the use of the silver salts in photography, etc.

Teachers wishing to secure directions for balancing any oxidation-reduction reaction not given in these lessons can secure the same from the writer by mail.

SUGGESTIONS ON CHAPTER XIV: THE PERIODIC SYSTEM.

Insist that students learn to make a sketch of the periodic system and to place any one of the common elements in the table.

SUGGESTIONS ON CHAPTER XV: THE FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY.

Most of the elementary text-books present some information on organic chemistry which should be read in this connection. The information they give is not sufficiently extensive, however, and hence it is supplemented here.

Contrary to what is indicated in the elementary text-books, it is advisable to stress the structural formulae of organic compounds.

Every student should know the structures of the main types of compounds.

Teachers who have not studied organic chemistry should study *Outlines of Organic Chemistry* by J. F. Moore, published by J. Wiley & Sons. This is a small, very readable book "designed especially for the general student."

It is advisable to have copies of the book entitled Elementary Applied Chemistry, by Lewis B. Allyn (Ginn & Co.) at hand so that the students may be referred to it for some optional exercises. A few of these exercises will serve to heighten his interest in the subject. The nature of most of these exercises is such, however, that an extensive use of this book is not advisable: most of the exercises are qualitative tests which do not teach any principles, and most of them have to be performed without being understood by the student.

SUGGESTIONS ON CHAPTER XVI: APPLIED ORGANIC CHEMISTRY.

Nothing special need be said here except that, for lack of time, portions of this chapter may be omitted.

Collateral reading on foods, digestion, and textile fibres may be assigned in Snell, *Household Chemistry* (Macmillan). This book presents in its latter half a splendid, extensive treatment of these topics. The first part of this book attempts to present the important parts of inorganic chemistry, but it does it in a manner which is not desirable.

SUGGESTIONS ON CHAPTER XVII: SIMPLE EXPERIMENTS FOR ILLUSTRATING THE VOLUME RELATIONS OF REACTING GASES.

As mentioned before the subject matter of this chapter is not absolutely necessary as a part of a course in elementary general chemistry and none of this subject should be given *unless illustrative experiments on this subject are actually carried out before the student.* This chapter presents some exceedingly simple experiments on this subject, which may be performed by all the students. When the subject is approached through these experiments, then a short presentation of the subject of molecular weights at the end of the course is quite desirable. However, this subject is quite "deep" for elementary students, and hence it is advisable not to dwell on the subject too long in the hope of enabling the students to understand it fully. The only procedure that has any chance for success is a brief concrete illustration of how molecular weights were first ascertained and therefore this illustration is presented here.

ADDITIONAL LIST OF CHEMICALS AND APPARATUS NOT LISTED IN PART I OF THIS BULLETIN, BUT WHICH ARE REQUIRED FOR THE EXPERIMENTS IN THIS BOOK.

½ lb. Bismuth Nitrate ..... $ 1.25
1 oz. Methyl Orange ..... .25
1 lb. Chloride of Lime (buy locally) ..... .15
1 gallon Cottonseed Oil (buy locally) ..... .50
1 quart Linseed Oil (buy locally) ..... .20
1 gallon Crude Oil (buy locally) ..... .20
2 liters $N/1H_2SO_4$ 1.00
1 lb. Fuller's Earth ..... .10
1 gallon Creosote Oil ..... .75
(Buy this from any one of the *Creosote Works,* situated at Galveston, Texarkana, and Beaumont, or from the Santa Fe works at Somerville, the Katy works at Greenville, or the Southern Pacific works at Houston. Crude carbolic acid of a specific gravity 1.03 to 1.05 can be bought locally and can be used instead of creosote oil.)
10 Alundum filters 4.50
(From the Norton Co., Worcester, Mass.)
Dr. Graefe's Calorimeter for gases—complete 25.00
(This can be obtained from Eimer and Amend, New York City, as listed in Cat. C, No. 2648D. The calorimeter vessel alone can be made by a local tinner for about $3.00, or it can be bought from Eimer and Amend for about $10.00. In either case a good thermometer for about $3.00 must be obtained. It should be divided into .1 degree centigrade, and should have a range from 15° to 40° C.)
12 inches of thin, flat rubber tubing, 2 inches wide ..... .15
(This is to be used in connection with the Alundum filters.)
Magneto Generator 5.00
(This is to be purchased only if there is no source of electric current convenient. It can be obtained from the Central Scientific Co., Chicago, Ill., as listed in the 1914 catalogue, No. 2276.)
1 Hydrometer having a range of .700 to 1.000 ..... 1.60
1 Hydrometer having a range of 1.000 to 1.200 ..... 1.60
Westphal's Specific Gravity Balance 15.00
2 quarts Carbon Tetrachloride 1.00
1 Babcock Milk Tester, any commercial form,—can be obtained locally, or perhaps borrowed for the one occasion on which it is needed here.

The indicators *methyl orange* and *phenolphthalein* are prepared for use in titrations as follows: (a) Methyl orange—dissolve ½ gram in 500 c.c. of water; (b) Phenolphthalein—dissolve 1 gram in 100 c.c. of 95 per cent alcohol.

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